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Thermodynamic Studies on Phase Transitions of Potassium Thiocyanate and Ammonium Thiocyanate Crystals

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Heat capacities of KSCN and NH_4SCN crystals were measured by adiabatic calorimetry in the temperature range between 13 K and the melting points. Molar volume of NH_4SCN was also determined above room temperature. Entropy change for the II-I transition of KSCN (414.54 K, essentially higher order but accompanied with the first order component) is 6.26 J K^{-1} mol^{-1} (=1.09 R ln 2), which is of similar magnitude with our previous value (*Bull. Chem. Soc. Jpn.*, **36**, 1025 (1963)). Entropy change for the III-II transition of NH_4SCN (360.1 K, first order) is 10.01 J K^{-1} mol^{-1} and apparent entropy change for the II-I transition of NH_4SCN (392.8 K, higher order) is 2.85 J K^{-1} mol^{-1} (=0.49 R ln 2) in spite of possibly similar nature of the transition with the II-I transition of KSCN. A possibility has been suggested that the entropy change might be approximately R ln 2 if the transition was not interfered with the III-II trasition and the premelting.

In the previous paper,[1] thermodynamic studies were reported which had been carried out on potassium thiocyanate (KSCN) crystal by use of a conduction calorimeter above room temperature in combination with the infrared studies and its apparently higher order transition at 414.5 K was interpreted in terms of orientational disorder of thiocyanate ions in the higher temperature phase††† of the crystal. In parallel with these studies X-ray diffraction study was also reported by Yamada and Watanabé.[2]

In the present paper we have studied the thermodynamic behavior of NH_4SCN crystal and reinvestigated that of KSCN crystal. Ammonium thiocyanate crystal, which consists of two kinds of polyatomic ions, undergoes two phase transitions below the melting point.††† A significant volume decrease on heating was observed for the III-II transition by Bridgman in his high pressure experiments.[3] X-Ray diffraction study on phase III showed that the crystal is monoclinic with four pairs of ions per unit cell ($\beta=97.4°$, $a=0.43$ nm, $b=0.72$ nm, $c=1.30$ nm) arrayed in a layered structure.[4] A thermoanalytical study on the system KSCN–NH_4SCN showed that both compounds formed solid solution in phases I and II over the entire composition range.[5] Hence, both crystals are possibly isomorphous with each other in these phases and the II-I transitions in these crystals are possibly of similar nature. Pressure dependence of the II-I transition temperature for these crystals were studied and its thermodynamic implication was discussed.[6,7]

Heat capacity measurements for ammonium thiocyanate crystal above room temperatures by conduction calorimetry and for ammonium thiocyanate and potassium thiocyanate crystals below 300 K by adiabatic calorimetry had been completed before 1969.[8] Heat capacities obtained by conduction and adiabatic methods for the both compounds showed discrepancies at 300 K. Subsequently, Vanderzee and Westrum reported the results of heat capacity measurements below 340 K for both salts.[9] Their results also showed discrepancies with our results obtained by conduction calorimetry. Further measurements of heat capacities above ordinary temperature were carried out by adiabatic calorimetry for these crystals, in order to examine the validity of our previous conclusion on the phase transition of potassium thiocyanate and to elucidate the mechanism of phase transitions of ammonium thiocyanate. In this paper, heat capacities of these crystals at temperatures above 13 K and below the melting points and molar volumes of ammonium thiocyanate above room temperatures are reported.

Experimental

Materials. Commercial potassium thiocyanate (Wakō, special grade) was purified by repeated recrystallization from methanol solutions followed by drying under vacuum (≈0.1 Pa) at 373 K and loaded into the calorimeters under dry nitrogen atmosphere. The nitrogen was exchanged with helium, when helium was used as heat exchange gas.

Commercial ammonium thiocyanate (Wakō, special grade) used for calorimetry and dilatometry was purified by repeated crystallization from 50% aqueous methanol solution and methanol solutions. The crystal was dried under vacuum (≈0.1 Pa) through heating and cooling cycles around the III-II transition temperature. In spite of the precaution, examination of the heat capacity behavior indicated the presence of a small amount of methanol occluded in the crystals by showing an excess heat capacity at 176 K with magnitude similar to that observed by Vanderzee *et al.*[9] The anomaly was attributed to the melting of CH_3OH-NH_4SCN eutectic mixture by them. Loading into the calorimeters and substitution of nitrogen with helium were carried out as for the potassium salt.

Calorimetric Procedures. Measurements between 13 and 300 K for both compounds were carried out by adiabatic calorimetry using a cryostat, a gold calorimeter cell, and a control system described elsewhere.[10] The calorimetric sample of potassium thiocyanate had a mass corrected to buoyancy of 30.141 g and its heat capacity ranged from 35% of the total at 13K to 59% at 300 K. The contribution from nitrogen (heat exchange gas except in series IV of Table 1) including the effects of its melting and vaporization or that from helium (heat exchange gas in series IV) was subtracted properly. The mass of the calorimetric sample of ammonium thiocyanate corrected to buoyancy was 22.227 g and contri-

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††† Crystalline phases are denoted as I, II, (and III) from higher temperature side for both crystals.

bution of its heat capacity to the total ranged from 44% at 13 K to 66% at 298 K. Contribution of helium packed in the calorimeter was corrected properly. The original heat capacities for both compounds, determined in 1968 in terms of NBS-55 temperature scale below 90 K and in terms of International Temperature Scale of 1948 (IPTS-48) between 90 and 300 K, were converted to the values in terms of IPTS-68 in this paper.[11,12]

Measurements above 300 K for both compounds were performed by adiabatic calorimetry using a calorimetric system described elsewhere,[13] and a gold calorimeter-cell equipped with eight internal radial vanes and two silver shields. Temperature was measured by a Tinsley type 5187-L platinum resistance thermometer calibrated in terms of IPTS-68 against a Leeds-Northrup type 8163 platinum resistance thermometer. Lead wires in the calorimetric system were replaced with copper wires (0.2 mm in diameter) covered with glass-fiber. The mass of calorimetric sample (corrected for buoyancy) was 32.799 g for the potassium salt and 23.485 g for the ammonium salt. Contribution of the heat capacity to the total was 46—50% for the former and 52—55% for the latter in the temperature range where no heat capacity anomaly was observed. Contribution from helium enclosed in the calorimeter was corrected properly.

Dilatometry. A glass dilatomer with internal volume of *ca.* 10 cm^3 was used. Confining liquid was mercury. The mass of ammonium thiocyanate crystal packed in the dilatometer was 6.262 g. Temperature of the dilatometer was detected by a copper-constantan thermocouple. Molar volume for phase III was calculated on the basis of the molar volume at 295 K obtained from X-ray diffraction data.[15] For other phases X-ray diffraction data[15] at 362 K was employed for the calculation.

Results and Discussion

Potassium Thiocyanate. Enthalpy increase per 1 K is presented in Tables 1 and 2 for temperatures below and above 300 K, respectively. Molar heat capacity was obtained by applying curvature correction and shown in Fig. 1 over the entire temperature range. The curves for both temperature ranges are smoothly connected with each other at 300 K. The molar heat capacity below 330 K is in agreement with the values reported by Vanderzee *et al.*[9] within 1%.

Relative enthalpy $[H^\circ(T)-H^\circ(400\text{ K})]$ plotted against temperature is shown in Fig. 2. Enthalpies from the three series of measurements are in good agreement with each other except for those above 414.5 K for Series VI, in which temperature increments around 414.5 K were small. A small but distinct discontinuity is observed at 414.54 K, which was assigned to the transition temperature as given in Table 3. A small discontinuity (0.20 cm^3 mol^{-1}) is found at the same temperature also in the molar volume *vs.* temperature curve as shown in Fig. 7. These findings indicate unambiguously that the transition is a higher order transition accompanied with the first order component as suggested by Klement.[7] The transition was interpreted as a higher order transition previously by the present authors[1] and by Yamada and Watanabé[2] and as a first order one with a small volume change by Bridgman.[3] Both conclusions are partly correct in view of the present findings.

As shown in Fig. 1, a straight line connecting the points at 300 and 438 K on the heat capacity curve was drawn for the estimation of a "normal" heat capacity in the transition region. Vanderzee and Westrum showed that the difference between experimental and calculated heat capacities of potassium thiocyanate crystal deviates from ±1% limits above 310 K.[9] This fact is in harmony with the present selection of 300 K as the lower temperature limit of the transition region. Transition enthalpy and entropy thus determined are given in Table 3 together with contributions from the

Table 1. Enthalpy increments per 1 K of potassium thiocyanate crystal below 300 K

$\frac{T}{\text{K}}$	$\frac{\Delta H/\Delta T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\Delta T}{\text{K}}$	$\frac{T}{\text{K}}$	$\frac{\Delta H/\Delta T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\Delta T}{\text{K}}$
	Series I		159.69	68.93	5.912
			165.57	69.85	5.850
12.81	1.109	3.473	171.39	70.74	5.793
15.94	2.312	2.775	177.15	71.68	5.736
19.23	4.075	1.627	182.85	72.50	5.684
20.84	5.186	1.619	188.51	73.32	5.633
			194.12	74.16	5.579
	Series II		199.68	74.96	5.535
			205.18	75.90	5.486
17.38	2.998	1.873	216.04	77.48	5.401
19.37	4.197	2.111	221.41	78.20	5.353
21.48	5.689	2.097	226.75	78.94	5.321
23.77	7.522	2.482	232.04	79.78	5.281
26.33	9.743	2.647	237.30	80.41	5.248
29.12	12.330	2.943	242.53	81.10	5.215
32.40	15.699	3.600	247.79	81.77	5.311
35.72	18.625	3.061	253.01	82.51	5.148
38.60	21.60	2.694	258.14	83.10	5.119
41.56	24.32	3.224	266.54	84.50	6.098
44.63	27.07	2.924	272.61	85.31	6.054
47.63	29.48	2.692	278.63	86.22	6.005
50.23	31.84	2.523	284.61	87.10	5.959
			290.54	88.00	5.914
	Series III		296.42	89.00	5.866
			301.17	89.83	3.641
71.11	45.22	3.432			
74.43	46.81	3.196		Series IV	
77.58	48.14	3.111			
80.65	49.49	3.033	24.87	8.527	2.801
83.65	50.60	2.971	27.92	11.230	3.311
86.59	51.72	2.913	31.31	14.467	3.542
89.32	52.74	2.854	34.18	17.389	2.214
92.15	53.57	2.810	36.75	19.752	2.948
94.94	54.50	2.768	39.94	22.86	3.460
99.03	55.76	5.433	43.21	25.85	3.095
104.41	57.33	5.303	46.17	28.45	2.831
109.65	58.75	5.189	48.90	30.74	2.639
114.79	60.00	5.093	52.01	33.14	3.588
119.84	61.20	5.006	55.47	35.65	3.350
125.55	62.42	5.336	58.72	37.88	3.167
130.84	63.53	5.256	61.82	39.87	3.027
135.42	64.44	3.895	64.78	41.83	2.905
139.93	65.33	5.136	67.63	43.39	2.805
145.04	66.28	5.077	70.40	44.78	2.721
149.14	67.06	3.145	73.08	46.12	2.649
153.20	67.80	4.987	75.70	47.22	2.592

Table 2. Enthalpy increments per 1 K of potassium thiocyanate crystal above 300 K

T / K	$\Delta H/\Delta T$ / J K^{-1} mol^{-1}	ΔT / K	T / K	$\Delta H/\Delta T$ / J K^{-1} mol^{-1}	ΔT / K
	Series I			Series IV	
317.40	92.26	3.007	413.03	254.9	1.716
320.37	92.89	2.993	414.21	775.6	0.709
323.33	93.70	2.978	415.31	291.3	1.562
326.26	94.95	2.957	417.40	118.85	2.726
329.25	95.09	3.340	420.08	114.42	2.776
332.55	95.45	3.326			
335.83	97.07	3.294		Series V	
339.09	96.43	3.302			
342.34	98.05	3.272	301.27	88.99	6.713
345.76	99.32	3.706	305.85	89.72	3.023
349.42	100.06	3.687	308.85	90.25	3.015
353.07	101.21	3.663	311.82	91.20	2.995
356.68	102.55	3.636	314.79	91.59	2.987
	Series II			Series VI	
363.83	104.43	3.606	406.60	158.74	1.562
367.37	106.53	3.553	408.10	167.29	1.514
370.86	108.25	3.516	409.54	178.49	1.455
374.32	110.09	3.481	410.91	193.79	1.381
377.75	112.20	3.446	412.19	220.0	1.272
381.13	114.56	3.409	413.34	266.3	1.117
384.42	117.82	3.353	414.05	356.3	0.429
387.72	119.32	3.330	414.39	568.0	0.296
390.96	124.68	4.249	414.53	4404	0.045
394.17	127.41	3.211	414.55	4176	0.047
397.30	132.39	3.142	414.63	939.6	0.191
400.36	138.25	3.066	415.78	125.47	2.340
403.37	146.30	3.178	418.10	116.88	2.425
406.43	158.43	3.030	420.46	113.87	2.456
			422.71	112.73	2.461
	Series III		425.12	110.25	2.487
			427.53	109.53	2.493
408.11	168.35	2.920	429.93	109.25	2.494
410.85	194.18	2.668	432.23	108.86	2.497
413.21	271.4	2.130	434.62	107.82	2.506
414.62	942.2	0.774	437.03	108.44	2.498
416.66	119.03	3.531	439.42	108.92	2.490
420.15	114.51	3.601			
423.70	110.40	3.661			

first order component of the transition. The total entropy change of 6.26 J K^{-1} mol^{-1} is equal to 1.09 $R \ln 2$. The previous conclusion of the present authors[1] that the transition entropy may be interpreted principally in terms of two-fold orientational disorder of thiocyanate ions in phase II need not be altered at all.

Volume thermal expansion coefficient was calculated from the dilatometric data given in Appendix. Plots of the heat capacity below the transition temperature against the thermal expansion coefficient is shown in Fig. 3. The plots below 412.2 K was approximated with a straight line as shown in the figure. Pressure dependence of transition temperature $(\mathrm{d}T/\mathrm{d}p)_{\mathrm{tr}}$ was

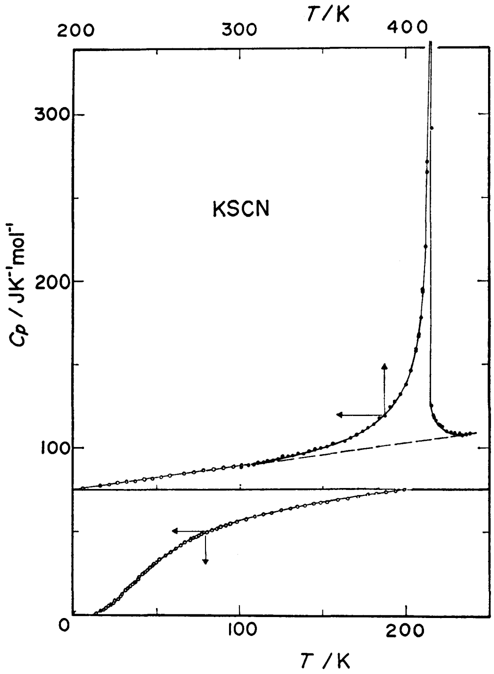

Fig. 1. Molar heat capacity of potassium thiocyanate crystal in the regions 12—300 K(○) and 300—410 K(●). Estimated normal heat capacity is drawn with a broken line.

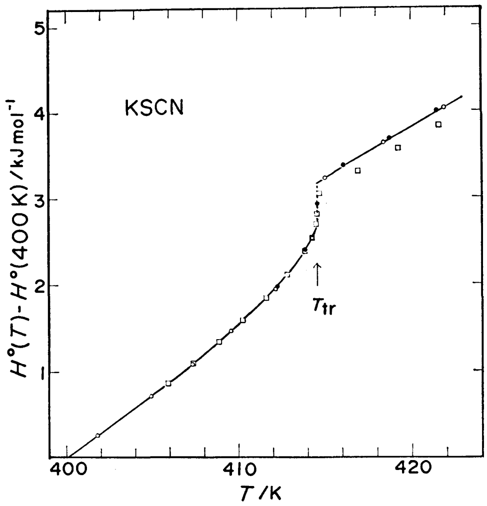

Fig. 2. Relative enthalpy $[H°(T)-H°(400\text{ K})]$ of potassium thiocyanate crystal around the II-I transition temperature.

○: Series II and III, ●: Series IV, □: Series VI.

Table 3. Transition temperatures, enthalpies, and entropies of potassium thiocyanate and ammonium thiocyanate crystals

Crystal	Transition	T / K	ΔH_{tr} / kJ mol^{-1}	ΔS_{tr} / J K^{-1} mol^{-1}
KSCN	II-I	414.54±0.02	2.53 (0.50)[a]	6.26 (1.21)[a]
NH_4SCN	III-II	360.1 ±0.1	3.61±0.03	10.01±0.08
	II-I	392.8 ±0.1	1.14	2.85

a) Contribution from the first order component.

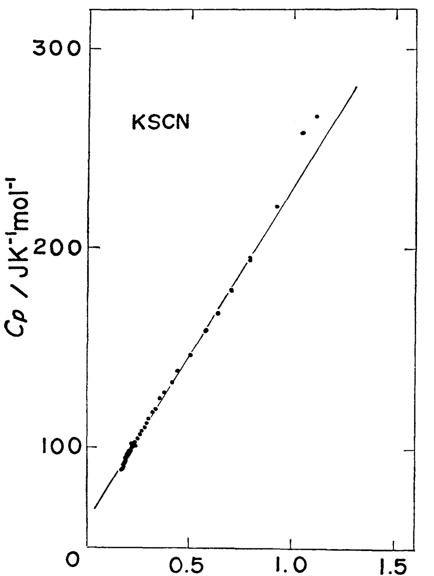

Fig. 3. Molar heat capacity *vs.* thermal expansion coefficient plot of potassium thiocyanate crystal below 414.5 K.

calculated from the slope of the straight line on the basis of the Pippard's relation,[14]

$$C_p = \left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\mathrm{tr}} V_{\mathrm{m}} T_{\mathrm{tr}} \alpha + \text{const},$$

where C_p, the molar heat capacity, V_{m}, the molar volume, α, the thermal expansion coefficient and T_{tr}, the transition temperature. The calculated value for $(\mathrm{d}T/\mathrm{d}p)_{\mathrm{tr}}$ is 0.134 K MPa^{-1}, while the observed value[6] is 0.172 K MPa^{-1}.

For the first order component of the transition, the Clausius-Clapeyron equation was applied with the volume change of 0.20 cm^3 mol^{-1} and the entropy change of 1.21 J K^{-1} mol^{-1}. The calculated value for $(\mathrm{d}T/\mathrm{d}p)_{\mathrm{tr}}$ is 0.165 K MPa^{-1}, which is rather in good agreement with the observed value.[6]

Ammonium Thiocyanate. Plot of the molar volume against temperature is shown in Fig. 4. Molar volumes calculated from the X-ray diffraction data by Pistorius[15] is also shown in the figure. As stated above, the dilatometric values were calculated with reference to the X-ray diffraction data at 295.2 and 361.7 K. Agreement is especially good for the temperature dependence of molar volume in phase II. Part of the molar volume *vs.* temperature curve around the II-I transition temperature is enlarged and presented in the enclosed portion. It is not clear whether a discontinuity in molar volume is present at the transition temperature or not. In the III-II transition, a discontinuous volume decrease (*ca.* 6% of the molar volume) took place on heating. Significant superheating and supercooling were also observed as will be explained below.

Changing topics to the discussion of heat capacity data, the effect of thermal decomposition upon the heat capacity values will be given. One of the principal reactions which ammonium thiocyanate crystal undergoes at higher temperatures may be the dissociation reaction into gaseous ammonia and gaseous isothiocyanic acid:

$$\mathrm{NH_4SCN(c)} \longrightarrow \mathrm{NH_3(g)} + \mathrm{HNCS(g)}. \qquad (1)$$

The dissociation pressure comes up to 101.325 kPa at 443 K.[16] Now, for the dissociation effect molar heat capacities were corrected approximately by using the following equation:

$$\Delta C_p = \Delta H_{\mathrm{r}}^{\circ}(T)\cdot\frac{MV_{\mathrm{g}}}{2mRT}\left(\frac{\mathrm{d}p}{\mathrm{d}T}-\frac{p}{T}\right), \qquad (2)$$

where ΔC_p is the correction to molar heat capacity, m, the mass of the sample in the calorimeter, M, the molar mass, V_{g}, the volume available for the gaseous species in the calorimeter, and $\Delta H_{\mathrm{r}}^{\circ}(T)$, the standard enthalpy of reaction. In the derivation of the equation, the gases were assumed to be ideal and only the direct effect of the dissociation was taken into account. Here, V_{g} was found to be 18.0 cm^3. $\Delta H_{\mathrm{r}}^{\circ}(T)$ for each of the phases

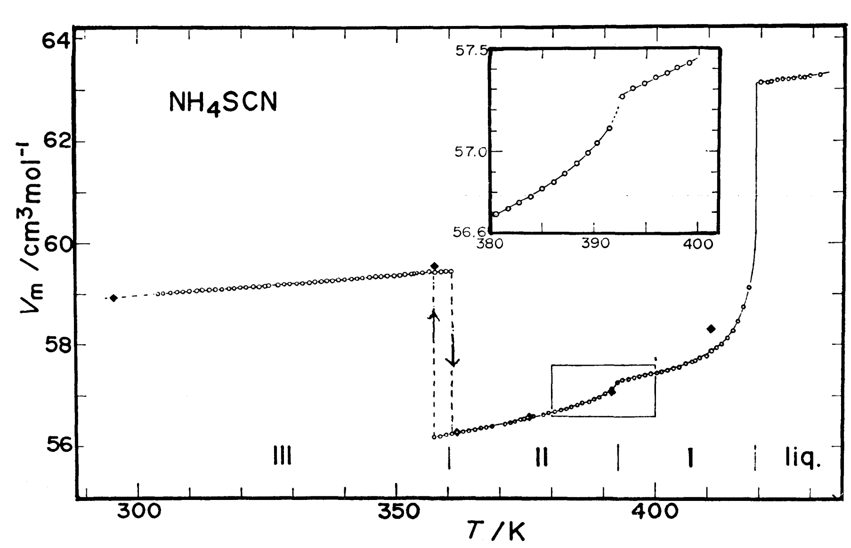

Fig. 4. Molar volume of ammonium thiocyanate in the crystalline and liquid phases.

○: Dilatometric data, ◆: X-ray diffraction data.[15]

was assumed to be independent of temperature for simplicity, *i.e.* 140 kJ mol^{-1} for the liquid phase, 149, 152, and 160 kJ mol^{-1} for the phases I, II, and III, respectively. These values were evaluated from standard enthalpies of formation at 298.15 K of the relevant species,[17] relative enthalpy $[H^\circ(T)-H^\circ(298.15\ \mathrm{K})]$ of ammonium thiocyanate, and molar heat capactites of the gaseous species.[17] The relative enthalpy of ammonium thiocyanate was calculated from the observed (uncorrected) molar heat capacities for the crystal below 400 K, while the molar heat capacities of the crystal above 400 K and of the liquid phase were assumed to be 130 J K^{-1} mol^{-1}. The observed enthalpies of transition as will be given below, and the enthalpy of melting (9.2 kJ mol^{-1}) determined by conduction calorimetry[8] were also utilized to estimate ΔH_r°. Dissociation pressure and its temperature dependence given in Eq. 2 were derived with reference to the dissociation pressure of 101.325 kPa at 443 K on the basis of the Van't Hoff's equation,

$$\ln p = -\frac{\Delta H_r^\circ(T)}{2RT} + \text{const.} \tag{3}$$

The correction term to molar heat capacity, ΔC_p, amounted to 0.10, 0.29, 0.61, and 1.21 J K^{-1} mol^{-1} at 360, 378, 393, and 407 K, respectively. Enthalpy increase per 1 K of the crystal corrected as above for the dissociation effect are tabulated for temperatures below 300 K and above 278 K in Tables 4 and 5, respectively. No correction was made upon the data of Table 4 for the effect of eutectic melting of NH_4SCN–CH_3OH mentioned above. Molar heat capacities were calculated by applying curvature correction for the

TABLE 4. ENTHALPY INCREMENTS PER 1 K OF AMMONIUM THIOCYANATE CRYSTALS BELOW 300 K

$\frac{T}{\mathrm{K}}$	$\frac{\Delta H/\Delta T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\Delta T}{\mathrm{K}}$	$\frac{T}{\mathrm{K}}$	$\frac{\Delta H/\Delta T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\Delta T}{\mathrm{K}}$
	Series I			Series IV	
101.84	57.71	3.243	13.11	1.812	3.328
105.06	59.20	3.181	16.16	3.208	2.822
108.22	60.63	3.129	18.66	4.755	2.162
112.23	62.38	4.902	20.96	6.305	2.458
117.07	64.50	4.785	23.41	8.106	2.451
121.81	66.45	4.683	26.10	10.255	2.957
			29.19	12.641	3.217
	Series II		31.95	14.896	3.315
			34.63	17.141	3.057
79.58	46.55	3.359	37.94	19.655	3.562
82.89	48.30	3.261	41.30	22.14	3.171
86.11	50.02	3.173	44.33	24.41	2.893
89.25	51.61	3.097	47.12	26.37	2.683
92.31	53.10	3.029	49.72	28.31	2.517
95.31	54.56	2.967	52.73	30.37	3.527
98.25	55.98	2.910	56.15	32.57	3.307
101.13	57.46	2.855	59.37	34.63	3.133
			62.42	36.69	2.990
	Series III		65.32	38.53	2.869
			68.17	40.10	2.770
124.55	67.69	5.776	70.91	41.81	2.717
130.26	70.01	5.638	73.57	43.33	2.599
135.83	72.21	5.515	76.14	44.73	2.531
141.29	74.35	5.403	78.64	46.04	2.469
146.64	76.43	5.300	81.08	47.37	2.413
151.89	78.48	5.204			
157.05	80.38	5.117		Series V	
162.12	82.09	5.040			
167.12	84.33	4.959	215.16	100.04	5.726
172.04	85.56	4.895	220.84	101.87	5.652
176.90	87.25	4.827	226.43	103.63	5.582
181.69	88.86	4.764	231.97	105.59	5.508
186.79	90.62	5.613	237.44	107.28	5.445
192.36	92.51	5.533	242.84	109.08	5.381
197.85	94.30	5.456	248.18	110.78	5.321
203.26	96.14	5.381	253.46	112.49	5.262
208.60	97.88	5.313	258.69	114.08	5.207
213.87	99.39	5.246	263.86	115.70	5.154
			269.33	117.48	5.851
			275.14	119.13	5.790
			280.89	120.93	5.726
			286.58	122.82	5.653
			292.22	124.15	5.612
			297.79	125.70	5.560

TABLE 5. ENTHALPY INCREMENTS PER 1 K OF AMMONIUM THIOCYANATE CRYSTAL ABOVE 300 K

$\frac{T}{\mathrm{K}}$	$\frac{\Delta H/\Delta T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\Delta T}{\mathrm{K}}$	$\frac{T}{\mathrm{K}}$	$\frac{\Delta H/\Delta T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\Delta T}{\mathrm{K}}$
	Series I		339.62	138.7	3.718
			343.30	139.1	3.712
298.84	124.9	3.635	346.94	140.2	3.695
302.44	126.1	3.622	350.56	141.3	3.679
306.05	126.8	3.607	352.71	140.0	1.910
311.40	129.0	7.130	354.54	141.9	1.888
316.73	130.6	3.542	356.37	143.0	1.879
320.25	131.1	3.529	358.19	143.2	1.877
321.96	131.7	3.489	360.74	142.7	0.607
324.31	132.0	1.216			
325.52	132.5	1.216		Series V	
326.73	133.1	1.214			
			368.06	145.8	3.390
	Series II		371.51	149.7	3.540
			375.03	157.8	3.560
320.55	132.3	2.011	378.41	168.7	3.314
322.58	132.4	2.117	381.67	171.2	3.285
326.53	135.1	1.977	384.92	179.9	3.174
328.46	135.2	1.978	387.96	201.4	2.969
			390.71	257.2	2.525
	Series III		392.47	374.0	0.994
			393.86	152.1	1.797
326.80	133.6	2.093	396.53	146.0	3.566
328.76	134.5	1.939	399.17	144.4	1.744
330.65	135.5	1.968			
332.56	134.6	1.964		Series VI	
334.46	137.8	1.946			
336.37	137.7	1.945	396.94	146.5	3.537
338.24	139.0	1.943	400.46	146.3	3.556
			403.90	148.5	3.525
	Series IV		407.20	154.6	3.444
			409.39	167.5	1.695
335.96	137.3	3.737			

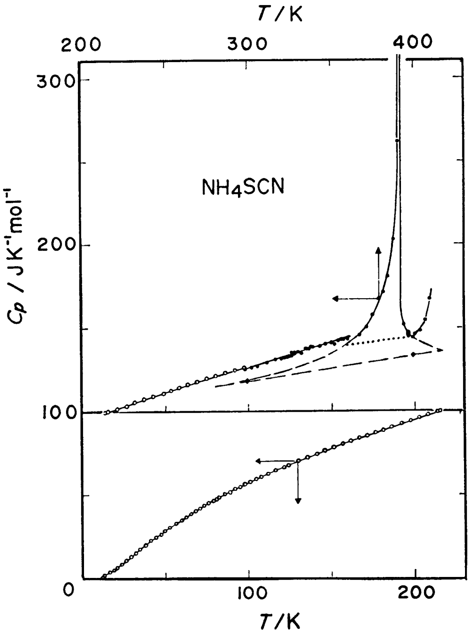

Fig. 5. Molar heat capacity of ammonium thiocyanate crystal. Experimental values are shown by empty and filled circles for the regions 13—300 K and 300—410 K, respectively. Estimated normal molar heat capacities at 300 and 400 K for phase II are shown by filled squares. For dotted and broken lines, see the text.

enthalpy increments and shown in Fig. 5 for the entire temperature range.

Another reaction to be taken into consideration will be the decomposition of ammonium thiocyanate in the solid state. The decomposition reaction in the liquid state was studied above 423 K by Kodama *et al.* in some detail.[24] The equilibrium composition of the reaction product at 423 K was 67% in ammonium thiocyanate, 30% in thiourea and 3% in other products. In the following discussion, only the isomerization

$$NH_4SCN \longrightarrow (NH_2)_2CS$$

will be considered. This reaction is exothermic at 298.15 K with the standard enthalpy of reaction of −9.6 kJ mol^{-1}, which has been calculated from enthalpies of formation of the both compounds in the solid states.[17] In the present study, the significant increase of temperature drift of the calorimeter in the cooling direction was observed above 402 K, which brought about difficulty in the precise measurement of molar heat capacity. Two molar heat capacity data above 402 K tabulated in Table 3 were obtained under the abnormal condition and would be influenced significantly with the isomerization reaction.

Increase in molar heat capacity above 402 K may be interpreted in the following way. Molar heat capacity of thiourea crystal at 298.15 K (108.91 J K^{-1} mol^{-1})[19] is considerably lower than that of ammonium thiocyanate crystal (*ca.* 125 J K^{-1} mol^{-1}) at the same temperature and the former crystal shows no phase transition between 298 and 400 K, while the latter undergoes two phase transitions in the same temperature range. Accordingly, the above-mentioned isomerization reaction as a solid state reaction would certainly continue to be exothermic up to 400 K. However, the system NH$_4$SCN–(NH$_2$)$_2$CS shows a eutectic point at 373 K with the mole fraction of thiourea of 0.3.[5] Thus a small amount of crystalline thiourea formed by the solid-state isomerization would melt immediately together with ammonium thiocyanate to give a melt rich in ammonium thiocyanate. From the analysis of equilibria between ammonium thiocyanate and thiourea in the liquid phase, enthalpy of reaction for the isomerization in the liquid state was determined to be −9.1 kJ mol^{-1}.[24] A thermochemical cycle involving both the species in the liquid and solid states shows that net change in enthalpy from ammonium thiocyanate crystal to thiourea liquid *via* thiourea crystal is almost neutral. On the other hand, ammonium thiocyanate in the liquid state would be converted to thiourea more rapidly than in the solid state, but the conversion is only of the order of 1% after 1 h even at 413 K.[18] Although the enthalpies of melting of ammonium thiocyanate and of isomerization in the liquid state into thiourea are of similar magnitude with opposite sign, realized net result would be the predominance of endothermic effect due to the melting of ammonium thiocyanate. Summerizing, the increase in molar heat capacity above 402 K may be interpreted in terms of premelting of ammonium thiocyanate crystal, triggered and accelerated by the isomerization into thiourea.

Transition temperature for III-II transition was determined to be 360.1$_5$±0.1 K by monitoring the temperature of the calorimeter under the adiabatic condition when the crystal transformed partially. Superheating and supercooling of the crystal were observed, when the crystal was heated up or cooled down through the transition range by a small temperature head between the calorimeter and the adiabatic jacket. Transition enthalpy and entropy are given in Table 3. The above-mentioned findings together with the discontinuous volume change in this transition reveal that the transition is of the first-order type. In phases I and II, the crystal forms mixed crystal with potassium thiocyanate crystal over the entire composition range[5] and they are possibly isomorphous. The crystal of ammonium thiocyanate in phase III is characterized with open structure with hydrogen bonding between essentially stationary ammonium ions and thiocyanate ions. In phase II, the orientation of the ammonium ions would be statistically disordered so that the crystal may be isomorphous with the potassium salt.

Application of the Clausius-Clapeyron equation for the III-II transition with the volume change of 3.42 cm^3 mol^{-1} (from X-ray diffraction[15]) and the entropy change of 10.0 J K^{-1} mol^{-1} (the present study) gave −0.342 K MPa^{-1} for $(\mathrm{d}T/\mathrm{d}p)_{\text{III-II}}$, which agreed with the observed value of Bridgman,[3] −0.334 K MPa^{-1}.

Transition temperature of the II-I transition of the ammonium salt was determined to be 392.8±0.1 K from the plot of relative enthalpy $[H°(T)-H°(361\ \mathrm{K})]$ against temperature. It is not certain from the relative enthalpy plot whether the transition is accompanied with a first-order component as observed for the potassium salt. Thermal expansion coefficient α of ammonium

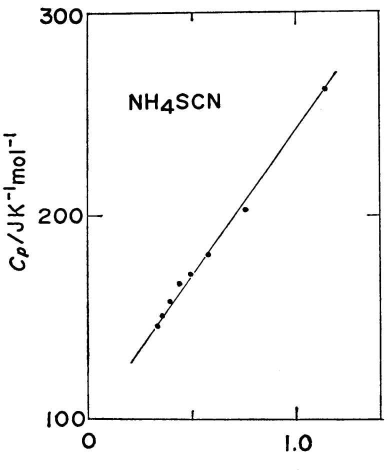

Fig. 6. Molar heat capacity *vs.* thermal expansion coefficient plot of ammonium thiocyanate crystal below 392.8 K in phase II.

thiocyanate crystal in phase II was calculated from the dilatometric data in Fig. 7 and the heat capacities were plotted against the thermal expansion coefficient as shown in Fig. 6. The plots below 385 K was approximated with a straight line. The value of $(\mathrm{d}T/\mathrm{d}p)_{\mathrm{II-I}}$ calculated from the slope of the straight line with the value of V_m of 57.0 cm^3 mol^{-1} on the basis of the Pippard's relation[14] is 0.155 K MPa^{-1}, while the observed value[7] is 0.126 K MPa^{-1}.

It is difficult to draw a reasonable "normal" molar heat capacity curve for phase II in Fig. 5. An obvious but tentative solution is to draw a straight line between the points at 360 and 398 K on the smoothed curve as shown by a dotted line in the figure. Transition enthalpy and entropy thus obtained are tabulated in Table 3. As stated above, the II-I transition in potassium thiocyanate and ammonium thiocyanate crystals should be similar in nature. Although the II-I transition of the ammonium salt is of essentially higher-order type as indicated in the heat capacity curve, the transition entropy 0.49 R ln 2 calculated as above is considerably lower than the expected value, R ln 2.

One possible interpretation of the apparent smallness of this transition entropy is that the crystal transforms from phase III into phase II which has been disordered to some extent with respect to the orientation of thiocyanate ions. A support to this is that thermal expansion coefficient of the ammonium salt at the lowest temperature in phase II is considerably higher than the corresponding value for the potassium salt at 300 K (see Figs. 3 and 6). The entropy change for the III-II transition is 10.0 J K^{-1} mol^{-1}, which is of sufficient magnitude to include a part of the contribution from the disordering process of thiocyanate ions in addition to the entropy change related with the orientational disorder of ammonium ions. In this respect, the adoption of the normal heat capacity as given above is in conflict with the supposition that orientation of thiocyanate ions has been disordered to some extent even at the lowest temperature in phase II.

This supposition leads to the suggestion that hypothetical heat capacity for phase II below the III-II transition temperature is lower than the one observed for phase III. Furthermore it is to be recalled that normal heat capacities have not been determined adequately for phase I by the interference with the premelting described above. Thus, the normal heat capacities for phase I should be lower than the observed values above 402 K.

Application of the Kopp's law using ("normal") heat capacities of ammonium chloride,[20] potassium thiocyanate, and potassium chloride[20] gave 125 and 153 J K^{-1} mol^{-1} for heat capacities at 300 and 400 K, respectively, which agree rather well with heat capacities of phase III observed at 300 K and extrapolated to 400 K and are therefore higher than expected for phase II.

Chihara and Nakamura[21] showed that heat capacity of ammonium chloride at 300 K was anomalously higher than the value calculated as a sum of Debye heat capacity and contributions from internal vibrations and harmonic (or anharmonic) vibration of ammonium ions. The anomaly had been pointed out earlier by Sakamoto.[22] Linear extrapolation of heat capacities of ammonium chloride at 500 and 600 K,[20] where the crystal is in the higher temperature phase, to 300 and 400 K gives 80 and 82 J K^{-1} mol^{-1} for heat capacities of ammonium chloride, respectively. Adoption of these values leads to 118 and 133 J K^{-1} mol^{-1} at 300 and 400 K, respectively, for ammonium thiocyanate.

Potassium and ammonium thiocyanate crystals are of cesium chloride type structure, while potassium and ammonium chloride crystals are of sodium chloride structure, in the relevant phases. This fact seems to lend support to the latter estimation of "normal" heat capacities.

A possible hypothetical "normal" heat capacity curve is thus drawn in Fig. 5 by a broken line, which is obtained by assuming that "normal" heat capacities are 118 and 133 J K^{-1} mol^{-1} at 300 and 400 K as shown by filled squares, respectively, and that it changes linearly between these temperatures. Anomalous heat capacities are also extrapolated smoothly to lower and higher temperatures as shown in the figure with broken lines. Hypothetical total entropy of transition for II-I transition thus obtained is 5.22 J K^{-1} mol^{-1}, which is equal to 0.91 R ln 2. Klement discussed the apparent entropy decrease with increasing polarizability of the cation observed for corresponding transitions of KSCN, RbSCN, NH_4SCN, and TlSCN.[7] However, the present analysis suggests a possibility that transition entropy for the ammonium salt would be compatible with the value of the isomorphous potassium salt, if the transition was not interfered with the III-II phase transition and the premelting.

Appendix

The molar volume of potassium thiocyanate crystal from 300 to 460 K has been reported only briefly in a previous paper.[23] Temperature dependence of the molar volume around 415.5 K (II-I transition temperature) is shown in detail in Fig. 7. Obviously, a small discontinuity of the molar volume can be observed in the small interval of 415.5—415.7

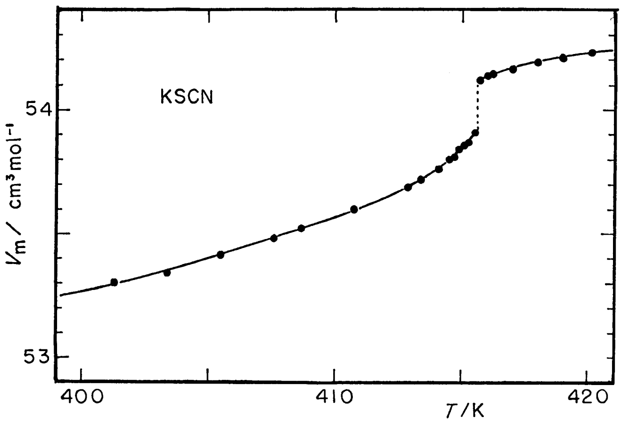

Fig. 7. Molar volume of potassium thiocyanate crystal around the II-I transition temperature.

K. Magnitude of the discontinuity amounts to 0.20 cm^3 mol^{-1}, which corresponds to 0.39% of the molar volume. The presence of the discontinuity had been shown implicitly as ΔV_t in Table 1 of the previous paper[23] before Klement pointed out from an analysis of molar volume data supplied by the authors.[7] However, the values of $\Delta V_t/V_t$, ΔV_t and t.p. given in the Table[23] are not correct and should read 0.39%, 0.20 cm^3 mol^{-1}, and 141.4 °C, respectively.

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