The heat capacity of NH$_4$Br from 265 to 550 K
The II-to-I transition[a]

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The heat capacity of NH$_4$Br has been measured from 265 to 550 K by precision adiabatic calorimetry. The results of these measurements were combined with existing low-temperature results to give thermodynamic functions up to 550 K. The nearly isothermal II-to-I transition at (412.66 ± 0.03) K has an entropy change of (8.710 ± 0.008) J K^{-1} mol^{-1}. The thermodynamic measurements of this study and existing sublimation pressures were used to determine an enthalpy of sublimation for NH$_4$Br of 189.0 kJ mol^{-1} at 298.15 K.

1. Introduction

The ammonium halides exist in several solid phases which are characterized both by orientational changes of the ammonium ion and by structural changes. Table 1 summarizes the crystallographic and thermodynamic information for ammonium bromide available prior to this work. Although accurate values exist for the heat capacities and thermodynamic properties of NH$_4$Br up to 300 K, none are available which enable careful elucidation of the thermodynamic properties above this temperature or characterization of the II-to-I transition. The present work was undertaken to remedy this deficiency. Precise heat-capacity measurements were made by adiabatic calorimetry from 265 to 550 K; this temperature range allowed for overlap with existing results and extended the measurements well into the phase I region.

2. Experimental

SAMPLE PREPARATION AND HANDLING

The ammonium bromide (Mallinckrodt Analyzed Reagent) was recrystallized twice from distilled water and purified by sublimation. The sublimed NH$_4$Br was again recrystallized from water, dried under vacuum, and stored in a desiccator.

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TABLE 1. Literature values of thermodynamic parameters of transitions between phases in NH_4Br

Crystal phase	IV ⟶	III ⟶	II ⟶	I[a]
	CsCl (ordered)	Tetragonal (ordered)	CsCl (disordered)	NaCl
T_t/K	107.5[b]	235.0[b]		410.95[d]
	108.5[c]	234.5[c]		410.35[e]
$\Delta S_t/J\ K^{-1}\ mol^{-1}$	1.122[b]	2.987[b]		(7.767)[f]
	1.121[c]	2.021[c]		(8.992)[g]
$\Delta H_t/J\ mol^{-1}$	122.6[b]	653.1[b]		3192[d]
	121.6[c]	473.9[c]		3690[h]

[a] X-ray diffraction, reference 1; neutron diffraction, reference 2; electron diffraction, reference 3. [b] See reference 4. [c] See reference 5. [d] See reference 6. [e] See reference 7. [f] Calculated from Bridgman data, reference 4. [g] Calculated from data of Pöyhönen and Arell, references 7 and 8. [h] See reference 8.

Microanalysis of the purified sample by Spang Laboratories gave (4.055 ± 0.005) mass per cent hydrogen, (14.37 ± 0.04) mass per cent nitrogen, and (81.73 ± 0.03) mass per cent bromine (theoretical; 4.122, 14.32, and 81.71 mass per cent, respectively).

CALORIMETER AND THERMOSTAT

An 83.69 g sample of ammonium bromide was loaded into a silver calorimeter (laboratory designation W-22). This calorimeter had a screw-type closure which utilized a stainless-steel knife edge and an annealed gold gasket. The loaded calorimeter was evacuated and sealed after the addition of 16.7 kPa of purified helium gas to facilitate thermal equilibration.

The heat-capacity measurements were made in the Mark IV adiabatic thermostat described elsewhere.[9] A Leeds and Northrup capsule-type platinum resistance thermometer (laboratory designation A-8), calibrated at the U.S. National Bureau of Standards against IPTS–48, was used for all temperature determinations; measurements of mass, current, potential, and time were also based on calibrations performed at N.B.S. The probable error of the heat-capacity values (except in the transition region where very small ΔT's were used) is considered to be 0.03 per cent. Equilibrium times after energy input were 30 min outside the transition and up to 13 h within it. This sluggishness, about ten times larger than previously encountered, required operation in a quasi-adiabatic mode in which the initial temperature of the shields was maintained throughout the energy input and for periods up to 30 min afterward. Adiabatic operation was then resumed over the remainder of the equilibrium period; adjustments were made for departures from adiabaticity.

3. Results

The experimental molar heat capacities (molar mass 97.9423 g mol^{-1} based on 1975 IUPAC atomic weights) determined in this study are presented in table 2.

TABLE 2. Molar heat capacity at constant pressure for NH$_4$Br

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
Series I		Series V		361.63	93.22	Series XIII	
315.95	89.66	376.81	94.27	371.58	93.89	290.80	86.61
328.37	90.88	392.77	94.98	381.46	94.43	301.40	87.99
340.65	92.01	400.49	95.35	391.30	94.93	311.88	89.24
352.81	92.88	406.26	95.48	Enthalpy Detn. F		322.23	90.42
364.87	93.72			441.11	80.63	378.99	94.39
376.83	94.39	Series VI		451.93	81.50	388.80	94.89
388.80	95.02	425.20	79.29			Enthalpy Detn. G	
400.68	95.65	427.85	79.54	Series X		439.27	80.58
409.96	195.5 [a,b]	430.51	79.79	399.35	94.85	450.00	81.50
413.57	1449 [a,b]			401.75	95.02	460.67	81.84
415.37	524 [a,b]	Series VII		404.16	95.31	471.27	82.51
422.71	93.01 [a,b]	393.76	95.02	406.57	95.40	481.80	83.18
435.41	80.50	Enthalpy Detn. D		408.98	95.60	492.25	84.27
Series II		449.16	81.25	411.39	95.77	502.44	84.85
396.24	95.06					512.75	85.60
Enthalpy Detn. A		Series VIII		Series XI		523.04	85.81
446.88	81.13	372.53	94.06	419.25	79.33	533.23	86.15
457.20	81.84	382.19	94.60	420.99	79.20	543.33	86.89
Series III		391.79	94.93	423.58	79.45	553.33	87.91
377.38	94.01	Enthalpy Detn. E				Series XIV	
385.05	94.47	440.93	80.67	Series XII		265.15	83.09
Enthalpy Detn. B		451.58	81.42	398.00	95.14	270.23	83.72
436.77	80.50			412.70	95.65	275.28	84.35
442.16	80.79	Series IX		412.79	−1079 [c]	280.31	85.06
Series IV		310.83	89.04	412.63	11720 [d]	285.31	85.60
371.24	93.47	321.17	90.16	412.69	20920 [e]	290.28	86.19
385.43	94.68	331.40	91.21	412.93	1870	295.22	86.94
Enthalpy Detn. C		341.55	91.92	414.42	300	300.15	87.53
440.47	80.63	351.62	92.59	419.22	81.46	306.66	88.28
				426.27	80.75	314.73	89.24
						Enthalpy Detn. H	

[a] Individual non-equilibrium determinations.

[b] In addition, several series of measurements were made on metastable phases as the following example shows. At time 0 the sample was at 553 K; by 12 h it had cooled to 401.5 K. It was heated to 420.3 by 14 h and cooled again to 406.6 K by 18 h. The temperature was maintained and energy inputs begun at 54 h with the following results:

T/K	409.72	412.38	414.77	416.91	419.31
C_p/J K^{-1} mol^{-1}	79.42	80.60	98.04	91.79	77.89

[c] Individual non-equilibrium determinations (superheated).

[d] $\Delta T = 0.072$ K.

[e] $\Delta T = 0.040$ K.

Temperature increments generally can be deduced from the adjacent mean temperatures. The values in table 2 are corrected for the heat capacity of the empty calorimeter and for differences in the amount of helium gas relative to the calorimeter as run empty. Curvature corrections were applied to compensate for the difference between the experimentally measured $\Delta H/\Delta T$ and the limiting value as the

temperature increments approach zero. The heat capacity of the sample represented from 60 to 70 per cent of the total measured heat capacity. Figure 1 shows the experimental heat capacities obtained in this study as well as measurements from previous studies up to 300 K.

Results from several determinations of the enthalpy of transition ΔH_t are summarized in table 3. Only the first five determinations were used in calculating the mean value of ΔH_t because the other determinations were made after an accidental heating of the sample to above 600 K. The subsequent decrease (0.152 per cent) in ΔH_t indicates that 0.0001 to 0.001 mol of NH_4Br had reacted with the silver-alloy brazing compound securing the closure to the silver vessel. This is consistent with the mass loss of the calorimeter and the local contamination of the sample found on unloading the calorimeter. However, no measurable change in heat capacity values occurred.

The experimental heat capacities, fitted to the polynomial:

$$C_p/\text{J K}^{-1} \text{ mol}^{-1} = \sum_{i=0} a_i x^i,$$

by computer, agreed satisfactorily with a large-scale plot of the experimental points. The heat capacity for crystal II can be expressed as a fifth-order polynomial in $x = \{T/\text{K} - 326.83\}/86.83$, and the coefficients a_i: 90.697, 8.590, -4.385, -0.2862, 1.812, and -0.686. For crystal I a sixth-order polynomial in
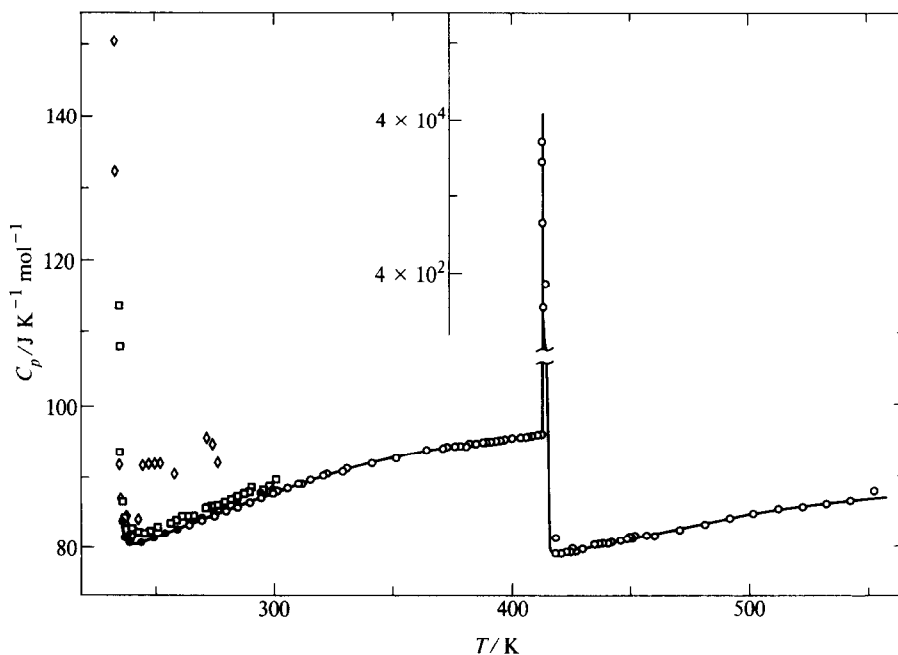

FIGURE 1. Molar heat capacity of NH_4Br. $\diamondsuit$, Simon, von Simson, and Ruhemann;[10] $\bullet$, Cole;[5] $\square$, Sorai, Suga, and Seki;[4] and $\bigcirc$, this research.

TABLE 3. Molar enthalpy of transition determinations for NH$_4$Br

Determination	$\dfrac{T_1}{\text{K}}$	$\dfrac{T_2}{\text{K}}$	$\dfrac{H^\circ(T_2)-H^\circ(T_1)}{\text{J mol}^{-1}}$	$\dfrac{H^\circ(444\text{ K})-H^\circ(387\text{ K})}{\text{J mol}^{-1}}$
A	399.12	441.65	7197.3	8538.3
B	387.92	434.07	7654.6	8542.1
C	389.46	435.01	7582.2	8539.5
D	397.05	443.06	7503.2	8533.3
E	396.58	435.60	6949.6	8535.8
F [a]	396.21	435.67	6980.2	8525.3
G [a]	394.85	433.87	6968.5	8529.1
H [a]	385.81	436.30	7068.0	8525.3
			Mean:	8537.8 ± 3.4

$$\{H^\circ(\text{lattice, }444\text{ K})-H^\circ(\text{lattice, }387\text{ K})\}/\text{J mol}^{-1} = 4943.4 \pm 3.4$$
$$\Delta H_t/\text{J mol}^{-1} = 3594 \pm 4$$
$$T_t = 412.66\text{ K}$$
$$\Delta S_t/\text{J K}^{-1}\text{ mol}^{-1} = 8.710 \pm 0.008$$

[a] Determinations F, G, H are not included in the mean (see text).

$x = \{T/\text{K} - 485.00\}/69.50$ and coefficients a_i: 83.567, 5.192, 1.172, -3.594, -5.703, 3.096, and 4.452 satisfactorily describes the results. The thermodynamic functions presented in table 4 were derived through appropriate integration of the fitted polynomial. Values below 15 K were extrapolated with a Debye T^3 heat-capacity function. Between 15 and 26 K the thermodynamic functions were derived from heat-capacities reported by Seki et al.:[4] between 26 and 260 K Cole's[5] data were preferred because they agree more closely with our measurements. His C_p values are roughly 0.5 per cent higher than ours in this region while the values of Seki et al. are about 1.5 per cent higher. Professor Seki has been most accommodating about endeavoring to resolve the discrepancy, but no explanation of it is apparent.[11]

4. Discussion

Our direct determination of the enthalpy of the II-to-I transition, (3594 ± 1) J mol^{-1} at (412.66 ± 0.03) K, is in reasonable accord with the direct determination by Arell:[8] (3690 ± 62) J mol^{-1} at 410.35 K. He used a differential calorimetric method and adopted the transition temperature determined dilatometrically by Pöyhönen.[7] In 1916 Bridgman[6] found the transition energy to be 3192 J mol^{-1} at a transition temperature of 410.95 K. His method combined volumetric information from dilatometric studies with pressure–temperature measurements and applied the Clausius–Clapeyron equation. This method is considered to give accurate transition temperatures but somewhat unreliable transition energies because it requires extrapolation far outside the range of measured values.

Figure 1 and table 2 illustrate the sharpness of the transition; virtually no pre-transition effects are noted. The transition itself was extremely sluggish and experimentally difficult to delineate. It was this unusual behavior that required shield operation in the quasi-adiabatic mode described earlier.

TABLE 4. Molar thermodynamic functions of NH_4Br

$\dfrac{T}{K}$	$\dfrac{C_p}{J\,K^{-1}\,mol^{-1}}$	$\dfrac{S^\circ(T)-S^\circ(0)}{J\,K^{-1}\,mol^{-1}}$	$\dfrac{H^\circ(T)-H^\circ(0)}{J\,mol^{-1}}$	$\dfrac{-\{G^\circ(T)-H^\circ(0)\}/T}{J\,K^{-1}\,mol^{-1}}$
		Crystal IV		
10	0.60	0.20	1.506	0.05 [a]
15	2.00	0.67	2.577	0.17 [b]
25	7.45	2.85	52.5	0.75
		Crystal II		
260	82.42	99.62	13487	47.74 [c]
270	83.68	102.76	14317	49.72 [d]
280	85.02	105.81	15161	51.66
290	86.36	108.83	16017	53.58
273.15	84.10	103.72	14581	50.33
298.15	87.40	111.21	16726	55.13
300	87.65	111.75	16887	55.48
320	90.00	117.49	18664	59.17
340	91.88	123.01	20484	62.77
360	93.34	128.32	22338	66.76
380	94.43	133.39	24217	69.66
400	95.27	138.24	26112	72.97
412.66	20920	141.25 [e]	27322 [e]	75.04
		Crystal I		
412.66	20920	149.95 [e]	30911 [e]	75.04
420	79.08	151.34	31493	76.35
440	80.63	155.06	33091	79.84
460	81.92	158.66	34715	83.19
480	83.22	162.17	36367	86.40
500	84.68	165.60	38045	89.50
520	85.81	168.95	39752	92.50
540	86.44	172.17	41476	95.39

[a] Graphical interpolation using C_p/T against T^2 plot. This research.
[b] From data of Seki et al.[4] between 15 and 26 K.
[c] From data of Cole et al.[5] between 26 and 260 K.
[d] Above 270 K, this research.
[e] Assuming the transition to be isothermal.

The sample was observed to superheat, *i.e.* the low-temperature phase persisted above the established transition temperature, by 2 to 4 K on several occasions. Undercooling was more pronounced. When cooled from 145 K above the transition at about 15 K h^{-1}, the release of energy signaling the onset of the transition began more than 10 K below the established transition temperature. When cooled from less than 10 K above the transition at about 4 K h^{-1}, the energy release occurred from 5.5 to 8.5 K below the expected temperature. On one occasion when the sample had been cooled below the transition and subsequently heated, not only did no appreciable fraction of the usual energy absorption occur in the transition region, but the heat capacities observed were those of Phase I (see footnote *b*, table 2).

Thermal hysteresis associated with the structural transitions has been observed generally in the ammonium halides. The effect for the bromide appears to be intermediate between that for the chloride[7] and that for the iodide.[12] Stephenson[13] has found hysteresis to be associated with the IV-to-III transition in the deuterated ammonium bromide. As has been observed often with the structural transitions, the crystal shattered, apparently as a result of numerous passages through the transition. The sample loaded into the calorimeter consisted of particles 3 to 4 mm in size; the sample removed had been reduced to a fine powder.

Using literature sublimation pressure of NH$_4$Br and a third-law analysis made possible by our results, we calculate the enthalpy $\Delta_r H$ of the sublimation reaction by the following procedure. Values of the left-hand member of the following equation for each reactant were used to obtain coefficients A_i:

$$-\{G^\circ(T)-H^\circ(298.15\ \mathrm{K})\}\,T^{-1} = A_1 + A_2\,T^{-1} + A_3\,T^{-2} + A_4\,\log_{10}(T/\mathrm{K}).$$

The coefficients A_i and the stoichiometric coefficients for the reaction:

$$\mathrm{NH_4Br(c,\ II) = NH_3(g) + HBr(g)},$$
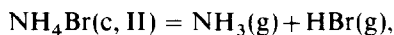
were used to calculate $\{\Delta_r G^\circ(T) - \Delta_r H^\circ(298.15\ \mathrm{K})\}\,T^{-1}$ at desired temperatures. The auxiliary data needed for these calculations were taken from the JANAF tables for HBr[14] and from Haar for NH$_3$.[15] For NH$_4$Br the functions listed in table 4 were converted to an $H^\circ(298.15\ \mathrm{K})$ basis. Literature values for the sublimation pressures p were used in $\Delta_r G^\circ = -2RT\ln\{p/(2 \times 101.325\ \mathrm{kPa})\}$ to obtain the changes in the Gibbs function $\Delta_r H^\circ(298.15\ \mathrm{K})$ was then calculated from

$$\Delta_r H^\circ(298.15\ \mathrm{K}) = \Delta_r G^\circ(T) - T\Delta_r[\{G^\circ(T) - H^\circ(298.15\ \mathrm{K})\}\,T^{-1}].$$

The enthalpies thus calculated are shown in table 5.

The agreement of the selected value, $(189.0 \pm 0.2)\ \mathrm{kJ\ mol^{-1}}$, with that obtained by Stephenson,[20] 189.0 kJ mol^{-1}, from solution data is spectacular. This reinforces the assumption of complete dissociation of NH$_4$Br vapor despite evidence for the presence of some undissociated species.[19,21-23]

TABLE 5. Third-law enthalpy of the sublimation reaction for NH$_4$Br(II) at 298.15 K

$\dfrac{\Delta_r H}{\mathrm{kJ\ mol^{-1}}}$	Method	Investigator
188.1 ± 0.4	Densi-tensimeter	P. M. G. Johnson[16]
188.3 ± 0.3	Isoteniscope	Smith and Calvert[17]
189.1 ± 0.2	Spiral manometer	Smits and Purcell[18]
189.0 ± 0.2	Isoteniscope	Callanan and Smith[19]
Selected value of $\Delta_r H$: (189.0 ± 0.2) kJ mol^{-1}		

REFERENCES

1. Bonilla, A.; Garland, C. W.; Schumaker, N. E. *Acta Cryst.* **1970,** A26, 156. Hovi, V.; Heiskanen, K.; Varteva, M. *Ann. Acad. Sci. Fenn.* **1964,** Ser. A6, No. 144. Hovi, V.; Paavola, K., Urvas, O. *Ann. Acad. Sci. Fenn.* **1968,** Ser. A6, No. 291. Pöyhönen, J.; Mansikka, K., Heiskanen, K. *Ann. Acad. Sci. Fenn.* **1964,** Ser. A6, No. 168.
2. Seymour, R. S.; Pryor, P. W. *Acta Cryst.* **1970,** B26, 1487. Egert, G.; Jahn, I. R.; Renz, D. *Solid State Comm.* **1971,** 9, 775.
3. Kolomiichuk, V. N.; Dvoryankin, V. F. *Soviet Phys.-Cryst.* **1964,** 9, 35. Kolomiichuk, V. N. *Soviet Phys.-Cryst.* **1966,** 10, 475.
4. Sorai, M.; Suga, H.; Seki, S. *Bull. Chem. Soc. Jpn.* **1965,** 38, 1125.
5. Cole, A. G. Ph.D. Thesis, Massachusetts Institute of Technology, **1952.**
6. Bridgman, P. W. *Proc. Am. Acad. Arts. Sci.* **1916,** 52, 91.
7. Pöyhönen, J. *Ann. Acad. Sci. Fenn.* **1960,** Ser. A6, No. 58.
8. Arell, A. *Ann. Acad. Sci. Fenn.* **1960,** Ser. A6, No. 57.
9. West, E. D.; Westrum, E. F., Jr. *Adiabatic Calorimetry from 300 to 800* K. In *Experimental Thermodynamics,* Vol. I, McCullough, J. P.; Scott, D. W.: editors. Butterworths: London. **1968.**
10. Simon, F.; von Simson, C.; Ruhemann, M. *Z. Physik. Chem.* **1927,** 129, 339.
11. Seki, S. Personal communication **1974.**
12. Stephenson, C. C.; Landers, L. A.; Cole, A. G. *J. Chem. Phys.* **1952,** 20, 1044.
13. Stephenson, C. C.; Karo, A. M. *J. Chem. Phys.* **1968,** 48, 104.
14. *JANAF Thermochemical Tables.* Dow Chemical Company: Midland, Michigan. **1965.**
15. Haar, L. *J. Res. Nat. Bur. Stand.* **1968,** 72A, 207.
16. Johnson, F. M. G. *Z. Physik. Chem.* **1909,** 65, 36.
17. Smith, A.; Calvert, R. P. *J. Am. Chem. Soc.* **1914,** 36, 1363.
18. Smits, A.; Purcell, R. *J. Chem. Soc.* **1928,** 2936.
19. Callanan, J. E.; Smith, N. O. *J. Chem. Thermodynamics* **1971,** 3, 531.
20. Stephenson, C. C.; Abajian, P. G.; Provost, R.; Wulff, C. A. *J. Chem. Eng. Data* **1968,** 13, 191.
21. Clementi, E. *J. Chem. Phys.* **1967,** 46, 3851; **1967,** 47, 2323.
22. Clementi, E.; Gayles, J. N. *J. Chem. Phys.* **1967,** 47, 3837.
23. Goldfinger, P.; Verhaegen, G. *J. Chem. Phys.* **1969,** 50, 1467.