Phase Transition in the Ammonium Bromide Crystal: The Thermal Motion of the Ammonium Ion*

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Ammonium halide crystals are well-known as typical substances which exhibit various kinds of polymorphism in the solid state. Among them, it has been established that in bromides[1-6] the following transformations occur:

NH_4Br: Phase I (NaCl) $\xrightarrow{411°K}$ Phase II (CsCl) $\xrightarrow{235°K}$ Phase III (tetragonal) $\xrightarrow{108°K}$ Phase IV (CsCl ?)

ND_4Br: Phase I (NaCl) $\xrightarrow{398°K}$ Phase II (CsCl) $\xrightarrow{215°K}$ Phase III (tetragonal) $\xrightarrow{169°K}$ Phase IV (CsCl)

It is noticeable that ND_4Br again takes the cesium chloride modification when it is cooled down through the tetragonal phase to a lower temperature. Stephenson and Adams[5] reported a new transition in ammonium bromide also at about 78°K on cooling and at about 108°K on warming. This seems to correspond to the transformation at 169°K in ND_4Br.[6] The possibility of the occurrence of this transition was also confirmed by Stevenson[7] through high-pressure experiments. Concerning the present material, Simon et al.[1] measured the heat capacity in the temperature range from −70°C to room temperature. Although Stephenson and Adams[5] reported briefly on the discovery of the new transition, as has been mentioned above, they have not yet published any detailed data on the heat capacities.

The purpose of our present investigation is to obtain detailed thermal data on ammonium bromide in the temperature range from 13°K to 305°K, and, in particular, to study the rotational motion or the torsional vibration of ammonium ions in crystals by analyzing our thermal and infrared data.

Experimental

Material. — A chemically pure-grade reagent ammonium bromide (Wakō Pure Chemical Industries, Ltd.) was recrystallized twice from distilled water and then sublimed under a vacuum of 10^{-4} mmHg at about 240°C. The specimen obtained was further recrystallized from distilled water and dried under a vacuum at about 50°C for several hours. About 30 g. of the specimen was then packed into the calorimeter cell.

For the measurement of the infrared absorption spectra, thin films of ammonium bromide on a rocksalt plate were used. The film was prepared by subliming the purified ammonium bromide through a loose glass wool plug onto a polished rocksalt plate under a pressure of about 10^{-2} mmHg at 110—130°C.[8]

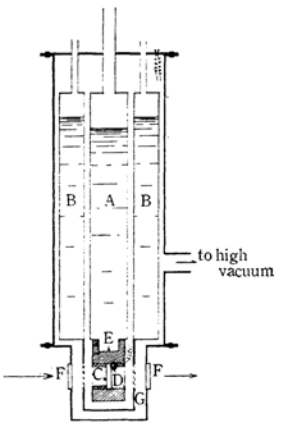

Fig. 1. Infrared absorption cell for use at low temperatures.
A, coolant reservoir (liquid He or H_2)
B, liquid N_2
C, rocksalt film-support
D, carbon resistance thermometer
E, copper cooling block
F, rocksalt window
G, radiation shield (liquid nitrogen temperature)

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1) F. Simon, Cl. von Simson and M. Ruhemann, *Z. physik. Chem.*, **129**, 339 (1927).
2) H. A. Levy and S. W. Peterson, *J. Am. Chem. Soc.*, **75**, 1536 (1953).
3) J. A. A. Ketelaar, *Nature*, **134**, 250 (1934).
4) J. Weigle and H. Saini, *Helv. Phys. Acta*, **9**, 515 (1936).
5) C. C. Stephenson and H. E. Adams, *J. Chem. Phys.*, **20**, 1658 (1952).
6) K. Clusius, A. Kruis and W. Schanzer, *Z. anorg. u. allgem. Chem.*, **236**, 24 (1938).
7) R. Stevenson, *J. Chem. Phys.*, **34**, 1757 (1961).
8) E. L. Wagner and D. F. Hornig, ibid., **18**, 305 (1950).

TABLE I. THE HEAT CAPACITY OF AMMONIUM BROMIDE

T_{av} °K	Approx. ΔT	$\Delta H/\Delta T$ cal./deg. mol.	T_{av} °K	Approx. ΔT	$\Delta H/\Delta T$ cal./deg. mol.
	Series I		212.29	2.389	20.294
21.89	3.010	1.329	217.01	2.335	20.989
24.57	2.360	1.744	221.93	2.485	21.801
26.76	2.015	2.039	226.81	2.398	22.961
28.99	2.485	2.381	229.28	2.534	23.811
31.57	2.715	2.786	231.66	2.260	25.058
34.55	3.281	3.137	233.82	2.064	28.555
37.84	3.368	3.714	235.96	2.211	25.826
41.01	3.013	4.165	240.93	2.627	19.755
53.05	2.879	5.751	243.56	2.636	19.621
55.85	2.734	6.068		Series II	
58.81	3.217	6.395	246.46	2.632	19.589
61.87	2.943	6.795	249.07	2.625	19.641
64.95	3.256	7.148	251.79	2.829	19.771
68.12	3.125	7.487	257.08	2.593	19.936
71.40	3.468	7.830	259.66	2.585	20.009
74.78	3.342	8.169	262.23	2.575	20.107
78.27	3.685	8.528	264.79	2.569	20.157
81.88	3.591	8.912	267.07	2.567	20.173
86.67	3.407	9.348	272.17	2.542	20.448
90.04	3.337	9.666	274.71	2.538	20.479
93.32	3.242	9.968	277.33	2.724	20.563
96.52	3.176	10.241	280.05	2.715	20.636
99.65	3.115	10.505	282.74	2.705	20.740
102.22	2.043	10.817	285.43	2.701	20.757
104.24	2.014	10.959	288.11	2.685	20.932
106.07	1.692	14.862	290.78	2.683	20.932
107.53	1.428	19.433	296.08	2.667	21.071
109.04	1.693	14.762	298.72	2.655	21.191
110.80	1.876	12.263	301.40	2.747	21.392
112.66	1.888	12.063		Series III	
114.53	1.883	12.069	98.53	1.599	10.561
116.85	2.800	12.193	100.12	1.587	10.652
119.61	2.770	12.351	102.08	2.352	10.819
122.52	3.084	12.540	104.40	2.321	11.012
125.56	3.046	12.740	106.30	1.529	11.181
128.71	3.294	12.956	107.80	1.516	11.322
131.95	3.248	13.203	109.29	1.503	11.442
135.31	3.513	13.461	110.76	1.491	11.578
138.78	3.464	13.722	112.21	1.479	11.708
142.17	3.419	13.970	113.65	1.465	11.865
145.55	3.380	14.177	115.08	1.447	12.094
148.89	3.335	14.450		Series IV	
152.18	3.294	14.705	100.75	2.346	10.665
157.87	2.122	15.053	103.04	2.313	10.863
160.05	2.272	15.249	104.93	1.522	11.062
164.55	2.236	15.619	106.38	1.455	11.965
168.97	2.198	16.024	107.54	1.045	20.548
173.70	2.475	16.373	108.58	1.229	15.931
178.46	2.338	16.768	109.84	1.406	12.605
183.10	2.301	17.183	111.23	1.435	12.101
187.77	2.487	17.615	112.98	2.152	12.051
192.71	2.476	18.086	115.10	2.143	12.075
197.57	2.401	18.548		Series V	
202.53	2.490	19.090	223.64	1.555	22.140
207.46	2.440	19.662	225.16	1.536	22.526

TABLE I (continued)

T_{av} °K	Approx. ΔT	$\Delta H/\Delta T$ cal./deg. mol.	T_{av} °K	Approx. ΔT	$\Delta H/\Delta T$ cal./deg. mol.
229.65	1.472	23.987		Series VII	
230.75	0.722	24.677	15.72	2.132	0.550
231.46	0.714	25.093	18.25	2.724	0.813
232.16	0.699	25.841	20.97	2.816	1.146
232.85	0.683	26.770	23.54	2.556	1.570
233.51	0.654	28.448	27.31	1.898	2.167
234.14	0.593	32.588	29.54	2.471	2.476
234.70	0.536	37.404	31.87	2.184	2.816
235.30	0.675	27.187	34.22	2.569	3.158
236.02	0.769	22.341	36.69	2.439	3.475
236.80	0.807	20.707		Series VIII	
237.61	0.821	20.134	40.75	3.378	4.132
238.43	0.825	19.969	43.94	3.067	4.538
	Series VI		46.85	2.833	4.932
15.82	3.357	0.529	49.43	2.392	5.282
18.52	2.296	0.840	51.94	2.708	5.601
			54.53	2.569	5.935

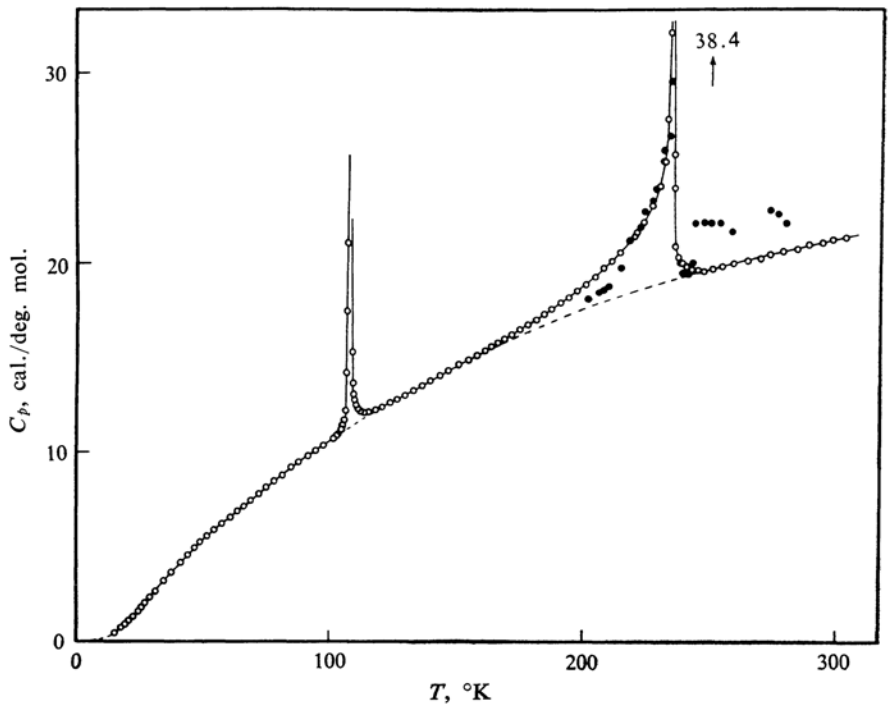

Fig. 2. Heat capacities of NH_4Br between the temperature range from 13°K to 305°K.
Broken lines represent "normal" heat capacity.
○ This work, ● Simon et al. (1927)

Apparatus.—The heat capacity measurements were carried out by the low-temperature automatic and adiabatic calorimetry techniques. A detailed description of them has already been given in the previous paper.[9]

The infrared spectra were recorded on a Nihon Bunkō Co. Double-beam spectrometer (model DS-402G). The cryostat for a low temperature measurement is illustrated in Fig. 1.

Results

The Heat Capacities of Ammonium Bromide.—The heat capacities of ammonium bromide were measured in the temperature range from

9) H. Suga and S. Seki, This Bulletin, 38, 1000 (1965).

13 to 305°K. The calorie defined as equal to 4.1840 absolute joules was used. The ice-point temperature was taken as 273.15°K. The calorimeter contained 28.5387 g. (0.29136 mol.) of ammonium bromide and helium gas for heat exchange. The experimental heat capacities, listed in Table I, are the ratios of the increase in enthalpy, ΔH, to the rise in temperature, ΔT, and are equal to the differential heat capacity, C_p, only when the correction for curvature is negligible. Also listed in Table I are T_{av}, the arithmetic mean of the initial and the final temperatures of each measurement, and the approximate temperature rise, ΔT. Our values for the heat capacities of ammonium bromide, together with those of Simon, von Simson, and Ruhemann,[1] are plotted in Fig. 2. We thus reconfirmed the new transition phenomenon reported by Stephenson, and also an unusually wide hysteresis effect associated with it. Here the broken lines are drawn as the "normal" heat capacity. The method of estimating these broken lines will be described later. We can see that the values given by Simon et al. are considerably scattered, so we are convinced that our values are much more accurate.

Anomalous heat capacities arising from the gradual phase transition at 235°K are reproducible in the repeated measurements. In the temperature region of normal heat capacity, including the anomalous region around 235°K, the calorimeter attained thermal equilibrium within a few minutes after an individual energy input. In the transition region at 108°K, however, the calorimeter established the thermal equilibrium only with difficulty, even after several hours. The approach to the thermal equilibrium in this region is compared with

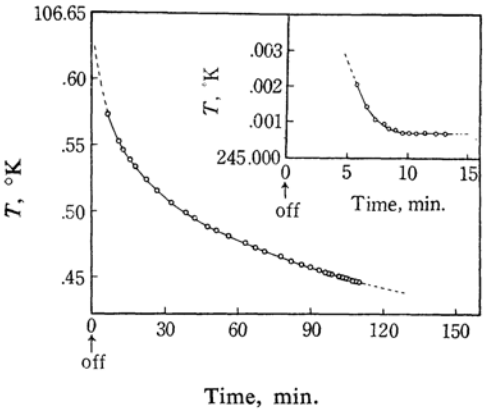

Fig. 3. Typical temperature drift curves showing behavior approaching to thermal equilibrium after an energy input. Upper one; ordinary temperature region. Lower one; transition region at 107.5°K.

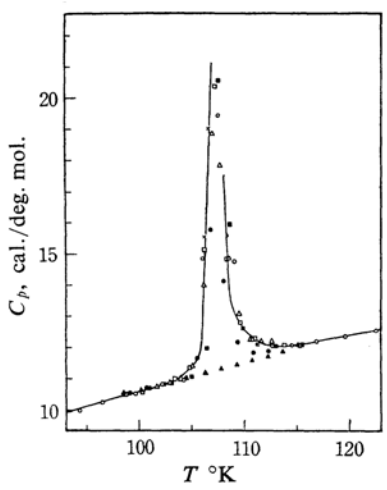

Fig. 4. Heat capacity of NH_4Br around the phase transition at 107.5°K.
○, the specimen was cooled down to 20°K; ●, to 75°K; △, to 69°K; ▲, to 97°K; □, to 70°K; ■, to 74°K; ×, to 63°K

that of a normal case in Fig. 3 for the sake of reference. The measurements of the heat capacity of ammonium bromide in the anomalous region around 108°K are plotted in Fig. 4. In this region the heat capacity values are not as accurate as in normal temperature regions.

The Thermodynamic Properties of Ammonium Bromide.—Smoothed values of the heat capacity, entropy, enthalpy, and Gibbs energy functions, and also of the standard thermodynamic values at 298.15°K, are listed in Table II. The differential heat capacity, C_p°, listed in the table, which is obtained from the observed values of $\Delta H/\Delta T$, was not corrected for curvature because of the small rise in temperature, ΔT.

The Anomalous Heat Capacities of Ammonium Bromide at 235°K and 108°K. — As is shown in Fig. 2, the heat capacity anomaly around 235°K covers a considerable temperature range, so there is some latitude in drawing a broken curve to obtain the normal heat capacity. To subtract the anomalous part, it is often useful to describe the heat capacity of a solid in terms of the Debye function. For this purpose, the experimentally-observed heat capacities, C_p, were represented by the apparent Debye characteristic temperature, Θ_D, with arbitrary degrees of freedom. The Debye characteristic temperature is known to be more sensitive than the heat capacity itself for the same amount of uncertainty in the heat capacity. Figure 5 shows the temperature dependence of the apparent Debye characteristic temperature, ${}_{12}\Theta_D$, the degrees of freedom

Table II. Thermodynamic properties of NH_4Br crystal (in cal./deg. mol.)

T °K	C_p°	S°	$\frac{(H^\circ - H_0^\circ)}{T}$	$-\frac{(G^\circ - H_0^\circ)}{T}$
10	(0.188)*	(0.1052)*	(0.0665)*	(0.0387)*
15	0.474	0.2273	0.1478	0.0795
20	1.027	0.4344	0.2940	0.1404
30	2.533	1.134	0.7881	0.3454
40	4.000	2.064	1.408	0.6557
50	5.353	3.103	2.063	1.040
60	6.582	4.190	2.716	1.474
70	7.686	5.289	3.378	1.911
80	8.705	6.382	3.955	2.428
90	9.665	7.464	4.537	2.927
100	10.584	8.530	5.096	3.434
107.5	27.5	Transition point		
110	12.535	9.831	5.880	3.951
120	12.382	10.89	6.405	4.486
130	13.061	11.91	6.890	5.018
140	13.813	12.90	7.358	5.546
150	14.546	13.88	7.812	6.069
160	15.234	14.84	8.255	6.587
170	16.069	15.79	8.689	7.101
180	16.908	16.73	9.123	7.610
190	17.814	17.67	9.556	8.115
200	18.805	18.61	9.993	8.616
210	19.980	19.55	10.44	9.114
220	21.482	20.52	10.91	9.611
230	24.165	21.52	11.41	10.11
235.0	38.4	Transition point		
240	19.799	22.52	11.96	10.61
250	19.690	23.37	12.27	11.10
260	20.020	24.15	12.56	11.59
270	20.338	24.91	12.85	12.07
280	20.647	25.66	13.12	12.54
290	20.947	26.39	13.38	13.00
300	21.246	27.10	13.64	13.46
298.15	21.194	26.97	13.59	13.38

* They were calculated from graphically extrapolated C_p values.

being assumed to be twelve. The broken lines in Fig. 5 are assumed to represent reasonably the course of the normal Debye characteristic temperature corresponding to the normal heat capacity. The enthalpy and entropy of transition, ΔH_{tr} and ΔS_{tr} respectively, the transition temperature, T_{tr}, and the transition range are given in Table III. The heat of transition was evaluated from the combined method of total heat input analysis and graphical integration.

Infrared Spectra at Low Temperatures.—The infrared spectra of thin, non-scattering films of ammonium bromide were obtained at 298°K (phase II), 100°K and 88°K (phase III), and

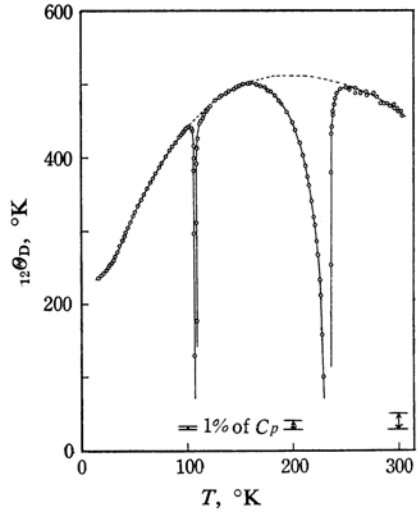

Fig. 5. The temperature dependence of the apparent Debye characteristic temperature, $_{12}\Theta_D$, where the degrees of freedom is arbitrarily chosen to be twelve.

40°K and 18°K (phase IV) respectively. The temperature of the specimen in the low temperature region was measured with an Allen-Bradley carbon resistance thermometer (nominal 47Ω, 1/10W.) which had been calibrated previously by using Clement-Quinell's equation. The two constants in this equation were determined by means of the resistance values at fixed temperatures, the boiling points of liquid helium and nitrogen. A copper: constantan thermo-couple, calibrated with a standard platinum resistance thermometer,[9] was used in the temperature region above the boiling point of liquid nitrogen.

The Wagner-Hornig assignments were employed for the analysis of the torsional frequency of the ammonium ion. The observed and inferred frequencies are summarized in Table IV. The spectrum of ammonium bromide in phase IV at 18°K is illustrated in Fig. 6 as an example. The combination band,

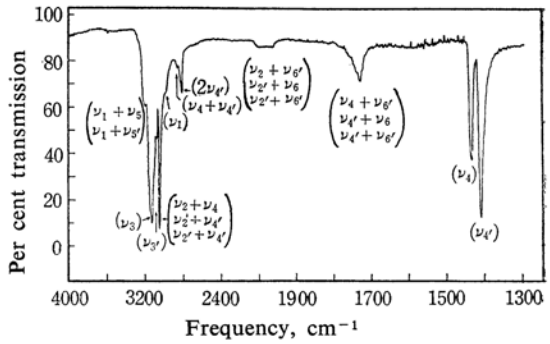

Fig. 6. Infrared spectrum of NH_4Br in phase IV at 18°K.

Table III. Temperatures, enthalpies and entropies of transitions, and transition ranges of NH_4Br crystal

	T_{tr} °K	ΔH_{tr} cal./mol.	ΔS_{tr} e. u.	Transition range
Lower transition	107.5±0.5	29.29	0.271	102—125°K
Upper transition	235.0±0.2	156.1	0.714	158—248°K

Table IV. Observed frequencies, assignments (after Wagner and Hornig), and inferred frequencies for NH_4Br, concerning torsional oscillation of ammonium ion

T, °K	298	100	88	40	18
Phase	II	III(a)	III(a)	IV	IV
		Observed frequencies (cm^{-1})			
ν_4'	1402	1411	1409	1411	1411
ν_4	1428	1436	1432	1435	1434
$\nu_4+\nu_6'$		1754(w)		1757(w)	1756(w)
$\nu_4'+\nu_6$	1742	1731	1732	1731	1734
$\nu_4'+\nu_6'$					
$2\nu_4'$	2804	2804	2810	2806	2815
$\nu_4+\nu_4'$		2851	2854	2852	2855
		Inferred frequencies (cm^{-1})			
ν_6 or ν_6'	(313)	(319)	(323)	(321)	(323)

(a) In these cases the specimen was cooled from room temperature down to these temperatures and did not experience the phase transition at about 78°K.
(w) Very weak shoulder.

(ν_4' or ν_4) + (ν_6' or ν_6), gets sharper gradually and the fine structures appear progressively as the sample is cooled.

Discussion

The degrees of freedom contributing to the heat capacity at a constant pressure, C_p, for the ammonium halide crystal may be the following: $6N$ degrees for translational freedom (lattice vibrations (C_v^L)); $9N$ degrees for internal vibrations (C_v^I); $3N$ degrees for torsional vibrations of ammonium ions (C_v^t); and C_p-C_v correction. The heat capacity, C_p, is then given by:

$$C_p=C_v^L+C_v^I+C_v^t+(C_p-C_v) \quad (1)$$

We should like to discuss each term on the right hand side of Eq. 1 separately.

C_p-C_v Correction.—The quantity measured is the heat capacity at a constant pressure; this is the basic result from which other quantities may be derived. The heat capacity at a constant volume, which is the quantity most suitable for comparisons with available theory, may be computed from the well-known thermodynamic relation:

$$C_p-C_v=\alpha^2VT/\chi \quad (2)$$

where α is the cubical coefficient of thermal expansion; V, the molar volume, and χ, the isothermal compressibility. Unfortunately, thermal expansion and compressibility data are incomplete in the present temperature region. Therefore, it is necessary to have recourse to the quasi-thermodynamic relation:

$$C_p-C_v\simeq AC_p^2T \quad (3)$$

where A is a constant. From Eqs. 2 and 3, the constant A is determined:

$$A\simeq\alpha^2V/\chi C_p^2 \quad (4)$$

The numerical value of the constant, $A=9.547\times10^{-6}$ mol./cal., was computed from the following values at 0°C:

$$\alpha^{10,11)}=16.20\times10^{-5}\ deg^{-1}$$
$$\chi^{12)}=6.188\times10^{-6}\ cm^2/kg.$$
$$V^{10,13)}=40.107\ cm^3/mol.$$
$$C_p=20.435\ cal./deg.\ mol.$$

The differences between C_p and C_v were calculated from Eq. 3.

Internal Vibrations in Ammonium Ions (C_v^I).—The contributions of the internal vibrations in ammonium ions to the heat capacity are usually best represented by the summation of the Einstein functions corresponding to the normal vibrational modes. That is:

$$C_v^I=\sum g_iE(\Theta_{E_i}/T) \quad (5)$$

where the summation is extended over the

10) V. T. Deshpande and D. B. Sirdeshmukh, *Acta Cryst.*, **14**, 353 (1961).
11) F. Simon and R. Bergmann, *Z. physik. Chem.*, **8**, 255 (1930).
12) P. W. Bridgman, *Phys. Rev.*, **38**, 182 (1931).
13) H. E. Swanson and R. K. Fuyat, NBS Circular 539, Vol. I, 353 (1953).

nine normal vibrational modes, the degeneracy, g_i, being taken from Wagner-Hornig's data[8] and $\Theta_{E_i}=h\nu_i/kT$. Their values are:

$\nu_1=3040\ cm^{-1}$ (degeneracy 1); $\nu_2=1640$ (2); $\nu_3=3130$ (3), and $\nu_4=1410$ (3).

Correction for Thermal Expansion. — The quantity, C_v, mentioned above corresponds to the heat capacity at a constant volume at each temperature. For comparisons with available theory, this quantity, C_v, must be reduced to a fixed volume at 0°K. The heat capacity at a constant volume less the contribution from internal vibrations is $C_v^L+C_v^t$. The quantity $C_v^L+C_v^t$ is represented by the apparent Debye characteristic temperatures, ${}_9\Theta_D(V_T)$, for nine degrees of freedom, as a function of the temperature. In order to reduce the ${}_9\Theta_D(V_T)$ values to the volume at 0°K, the following approximate formula is used:

$$ {}_9\Theta_D(V_O)/{}_9\Theta_D(V_T)=(\rho_O/\rho_T)^\gamma=(V_T/V_O)^\gamma \fallingdotseq 1+\gamma\Delta V/V_O \qquad (6) $$

where V_O and ρ_O are, respectively, the volume and density at 0°K, and γ is the Grüneisen parameter defined by Kittel[14] as follows:

$$ \gamma=\alpha V/\chi C_v \qquad (7) $$

For lack of data on the temperature dependence of the molar volume and the Grüneisen parameter for ammonium bromide, we assumed that the behavior of the temperature dependence for ammonium bromide would be similar to that for potassium bromide.[15] The absolute values of V_T and γ for ammonium bromide, which, of course, are different from those for potassium bromide, are calculated by multiplying the factors determined at 0°C. The magnitude of the correction for ammonium bromide is illustrated in Fig. 7.

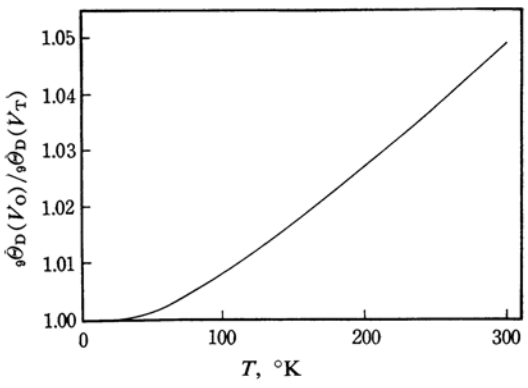

Fig. 7. The change of ${}_9\Theta_D$ with volume for ammonium bromide between 0°K and 300°K.

14) C. Kittel, "Introduction to Solid State Physics," Wiley, New York (1953).
15) B. Yates and C. H. Panter, *Proc. Phys. Soc.*, **80**, 373 (1962).

The Torsional Frequency of the Ammonium Ion and the Potential Barrier.—As has already been mentioned, the bromide in phase IV (below 107.5°K) may be regarded as of the CsCl-type on analogy with the neutron diffraction study[2] of deuterated ammonium bromide. In contrast to the same modification at room temperature, here the orientation of tetrahedral ammonium ions which are located at the center of a cube determined by eight halogen ions will be regularly ordered, and each ammonium ion will undergo torsional vibration about the two-fold symmetry axis of the ion in this modification.[2,16]

Recently Wulff[17] determined the barrier heights for the rotation of the methyl groups in some organic crystal by using the heat capacity data. Suga, Matsuo, and Seki[18] in our laboratory also estimated the torsional frequency of the CN^- ions in the potassium cyanide crystal and discussed the contribution of the rotational vibration to the heat capacity. In both these cases, however, no direct comparison of the frequency determined from the thermal data with that determined from the spectroscopic data has been made. In the present case the pure torsional vibration of ammonium ions is spectroscopically inactive, but fortunately the quite sharp bands arising from the combination band can be observed. Therefore, there is a distinct possibility of a comparison of the torsional vibration frequency of NH_4^+ ions derived from the analysis of the thermal data with those obtained from the infrared and Raman data. Moreover, the potential barrier height hindering the internal rotation of the ammonium ion about the two-fold symmetry axis obtained from the thermal data for the solid phase may also be compared with the NMR data of Gutowsky, Pake and Bersohn,[16] and Sachs.[19]

For these purposes, we have tried the following analysis for phase IV, working below 107.5°K, because of the complicated effects due to the phase transitions and the anharmonicity of vibrations at higher temperatures. The heat capacity, $C_v(V_O)$, calculated from the Debye temperature, ${}_9\Theta_D(V_O)$, in Eq. 6 consists of the "translational" effect for six degrees of freedom and the "torsional vibration" for three degrees of freedom, with the fixed volume at 0°K. As we have no "a priori" methods for separating the contribution arising from the

16) H. S. Gutowsky, G. E. Pake and R. Bersohn, *J. Chem. Phys.*, **22**, 643 (1954).
17) C. A. Wulff, ibid., **39**, 1227 (1963).
18) H. Suga, T. Matsuo and S. Seki, Preprint of the Symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July, 1963; This Bulletin, **38**, 1115 (1965).
19) A. M. Sachs, Ph. D. Thesis, Harvard University, 1949.

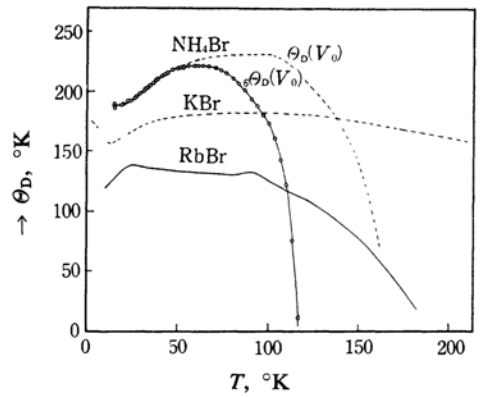

Fig. 8. Debye temperature of NH_4Br, KBr, and RbBr. Two curves for NH_4Br are explained in text.

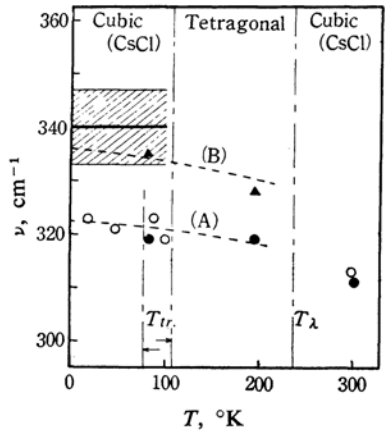

Fig. 9. Temperature dependence of the torsional frequency of ammonium ion.
○; The result from the analysis of infrared combination bands measured by us. ●; Infrared absorption data by Wagner and Hornig. ▲; Fundamental vibration frequency observed by the method of Raman spectroscopy by Krishnan. The shaded area represents the result from the analysis of thermal data.

torsional vibration and that from the translational motion, empirical assumptions are needed to calculate the torsional frequency and the potential barrier heights from the analysis of the thermal data. The first assumption is that the behavior of the temperature dependence of the Debye characteristic temperature, Θ_D, which corresponds to the "translational heat capacity" of ammonium bromide, may be similar to those of alkali halides, the crystal structure of which is of the CsCl-type at low temperatures, as in the case of ammonium bromide. Cesium bromide and chloride presumably satisfy this condition. As we have no suitable thermal data, however, about cesium bromide and cesium chloride in hand, the data for potassium bromide[20] and rubidium bromide[21] are used for the sake of comparison, although the crystal structure of both compounds is of the NaCl-type. The temperature dependences of the Debye characteristic temperatures of potassium bromide and rubidium bromide are reproduced in Fig. 8. The curves for both compounds are almost flat in the temperature range between 50 and 140°K for potassium bromide, and from 40 to 90°K for rubidium bromide, which means that the Debye model is applicable to these substances in these temperature ranges. The contribution to the heat capacity arising from the torsional vibration of the NH_4^+ ion may be approximately represented by an Einstein function, $E(\Theta_E/T)$, for three degrees of freedom with an empirically-chosen Θ_E. The "translational" or "lattice" heat capacity is then given by:

$$C_v^L = C_v(V_O) - E(\Theta_E/T) \qquad (8)$$

By trial and error, an adequate Einstein characteristic temperature, Θ_E, was determined, so that the curve of the temperature dependence of the apparent Debye temperature, Θ_D, corresponding to the heat capacity, C_v^L, might be flat in some temperature regions. The value of Θ_E determined in such a way is 490 ±10°K, which corresponds to the torsional oscillation of the NH_4^+ ion about its two-fold symmetry axes with the wave number of 340 ±7 cm^{-1}. The value of 340±7 cm^{-1} is consistent with the infrared data obtained by us and by Hornig et al.[8] and also with Raman data[22] extrapolated to the lowest temperature (see Fig. 9). One can see that in Fig. 9 there are rather small but significant differences between the infrared frequencies and those of Raman data. According to the discussion by Wagner and Hornig,[8] the torsional vibration of the ammonium ion, the ν_6 mode (triply degenerated in phases II and IV), splits into two components, $\nu_6(A_2)$ and $\nu_6'(E)$, in the tetragonal modification with the point group V_d (phase III), the latter mode (ν_6') being active in both the infrared and Raman spectra. The Raman frequencies[22] shown in Fig. 9 are the fundamental vibrations (ν_6' mode). The infrared data, however, are the results of the analysis of the complicated combination bands, whose assignments have not yet been fully established. In fact, the combination band gets sharper gradually, and

20) W. T. Berg and J. A. Morrison, *Proc. Roy. Soc.*, **A242**, 467 (1957).
21) K. Clusius, J. Goldmann and A. Perlick, *Z. Naturforsch.*, **4a**, 424 (1949).
22) R. S. Krishnan, *Proc. Ind. Acad. Sci.*, **A27**, 321 (1948).

the fine structures appear progressively when the specimen is cooled down to a lower temperature. This band has a width of about 50 cm^{-1} even at the lowest temperatures, so there is some uncertainty involved in resolving the combination bands into their component frequencies. In addition, the two spectra (infrared and Raman) should not be expected to coincide unless the coupling between ammonium ions is very weak.[8] Thus, one can not compare the absolute values of the two spectra directly until the complete assignment is established. Curve A in Fig. 9 represents approximately the temperature dependence of the torsional frequency as determined by an analysis of the combination bands. We can find that the frequency of the torsional oscillation shows almost no temperature dependence in the low temperature region. This fact justifies our treatment of the thermal data with a harmonic Einstein function. Curve B in the figure was drawn for the fundamental torsional oscillation by assuming the same temperature dependence as that of curve A in phase IV. The extrapolated fundamental values of the Raman data to the lowest temperatures compare quite well with those determined by the analysis of the thermal data. To check the results, it is also very desirable to measure the fundamental vibration in phase III (tetragonal modification) by the method of infrared absorption.

Now, we should like to proceed to the problem of the potential barrier. We have adopted the following potential function,[23] which is usually taken for such internal rotation or torsional oscillations as CH_3–, OH–, or C_2H_5– groups:

$$U(\phi)=\frac{1}{2}U_0(1-\cos n\phi) \tag{9}$$

where ϕ is the angle of rotation; n, the symmetry number; and U_0, the potential barrier height.

In the case of ammonium bromide, the symmetry number, "n," is approximately four, judging from the crystal structure. In phase II, the crystal structure of the ammonium bromide is of the CsCl-type. The orientations of the ammonium ions in this phase are found to be disordered. In the temperature region of phase III, the structure of the bromide is tetragonal[3,4] and the orientations are still in the ordered state. Below 107.5°K, the structure (phase IV) is of the CsCl-type and of the ordered orientations, analogous with the results of the neutron diffraction study[2] of deuterated ammonium bromide.

23) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, New York (1953).

As to the possible orientations of the tetrahedral ammonium ion which is located at the center of a cube determined by eight halogen ions, there are two possibilities. In the disordered phase II, these two orientations are equally probable and are distributed statistically at random over the whole lattice. On the other hand, in the ordered phase IV, all the ammonium ions have one and the same orientation.

In the disordered phase the symmetry number is exactly four, and the potential function is well represented by Eq. 9. In the ordered phase, however, the potential energy between two orientations is slightly different. The potential function, then, is better represented by:

$$U(\phi)=\frac{1}{2}U_0(1-\cos n\phi)+\frac{1}{2}U_1S\left(1-\cos\frac{1}{2}n\phi\right) \tag{10}$$

where S is an order parameter concerning the orientations of ammonium ions, and U_1 is the potential energy difference between the two orientations at 0°K.

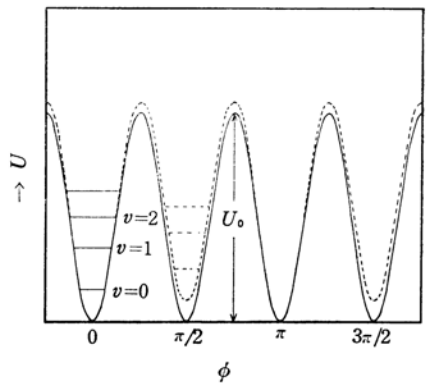

Fig. 10. Potential curves hindering rotation of ammonium ion about its two-fold symmetry axis.
——: $U(\phi)=(1/2)U_0(1-\cos 4\phi)$
----: $U(\phi)=(1/2)U_0(1-\cos 4\phi)+(1/2)U_1S(1-\cos 2\phi)$

The potential curves given by Eqs. 9 and 10 are illustrated in Fig. 10. Equation 10 requires knowledge about the temperature dependence of the S parameter. We assumed also the periodic function, with $n=4$, even in the ordered phases (phases III and IV). When the ions undergo torsional oscillation at a low temperature, the angle of rotation, ϕ, may be small. Then one can expand the potential function in a power series in ϕ as follows:

Table V. Potential barriers to rotation of the NH_4^+ ion in the ammonium halides (CsCl modification), in kcal./mol.

Compound	U_0(Eq. 14)	U_0(elec.)[a]	$U_0(\nu)$[b]	$U_0(T_1)$[c]
NH_4Br	4.00±0.16	3.73	4.18	4.65
NH_4Cl	6.24±0.26[d]	5.40	5.25	6.41

a) These values are entirely from an electrostatic calculation; Refs. 15 and 17.
b) These results obtained from the observed torsional frequencies; Ref. 15.
c) $U_0(T_1)=E$(activation energy from T_1)$+(3/2)h\nu_{obs.}$; Refs. 15 and 16.
d) This value is calculated by using Eq. 14 and the smoothed C_p-curve determined by Simon.[1]

$$U(\phi)=\frac{1}{2}U_0\left(\frac{n^2\phi^2}{2!}-\frac{n^4\phi^4}{4!}+\frac{n^6\phi^6}{6!}-\cdots\right) \tag{11}$$

By using the first-order perturbation theory, the energy levels of this anharmonic oscillator are calculated to be:

$$E_v=h\nu_0\left(v+\frac{1}{2}\right)-\frac{1}{2U_0}\frac{1}{4!}(h\nu_0)^2(6v^2+6v+3)+\frac{1}{2U_0^2}\frac{1}{6!}(h\nu_0)^3(20v^3+30v^2+40v+15) \tag{12}$$

and

$$\nu_0=\frac{n}{2\pi}\sqrt{\frac{U_0}{2I}} \tag{13}$$

where ν_0 is the frequency corresponding to the simple harmonic oscillator approximation; I is the moment of inertia of the ammonium ion, and v is the quantum number of the vibration.

If the torsional wave number $\nu=340\pm7\ cm^{-1}$, as determined from thermal data, is assumed to be the difference between $v=1$ and $v=0$, i.e., $h\nu=E_{v=1}-E_{v=0}$, then we have:

$$h\nu=h\left(\frac{n}{2\pi}\sqrt{\frac{U_0}{2I}}\right)-\frac{6h^2}{4!U_0}\left(\frac{n}{2\pi}\sqrt{\frac{U_0}{2I}}\right)^2+\frac{45h^3}{6!U_0^2}\left(\frac{n}{2\pi}\sqrt{\frac{U_0}{2I}}\right)^3 \tag{14}$$

and the potential barrier height, U_0, is 4.00±0.16 kcal./mol. On the other hand, a simple harmonic oscillator approximation using Eq. 13 gives the value of $U_0=3.52\pm0.16$ kcal./mol., and the potential function given by Eq. 10 gives a value of several per cent[24] smaller than 4.00±0.16 kcal./mol.

In calculating the potential barrier height, the numerical values of $I=4.778\times10^{-40}$ g. cm^2, the N-H distance=1.035Å,[16] and $U_1=kT_C$ ($T_C=235$°K) were used.

Gutowsky, Pake, and Bersohn[16] and Sachs[19] calculated the potential barriers to rotation of the NH_4^+ ions in the ammonium halides (CsCl modification) by measuring the spin-lattice relaxation time, T_1, by means of NMR studies. They also estimated the potential barrier by electrostatic calculation. The values of the potential barrier obtained are all summarized in Table V. We ourselves determined the value of U_0 for ammonium chloride with the above-mentioned technique by using the heat capacity data of Simon[25] and Eq. 14.

The Contribution of the Torsional Oscillation to the Heat Capacity.—If the periodic potential function given by Eq. 9 is assumed, the heat capacity, C_v^t, arising from the torsional vibration is a function of the temperature, T, of the symmetry number, n, and of the potential barrier U_0; i.e., $C_v^t=f(n, U_0, T)$.

Pitzer and Gwinn[23] have tabulated the thermodynamic functions for the contribution of the rotation. By using their table instead of the Einstein function, $E(\Theta_E/T)$, we have computed C_v^t. Figure 11 shows two cases of the temperature dependence of the "torsional" heat capacities, $f(n, U_0, T)$ and $E(\Theta_E/T)$.

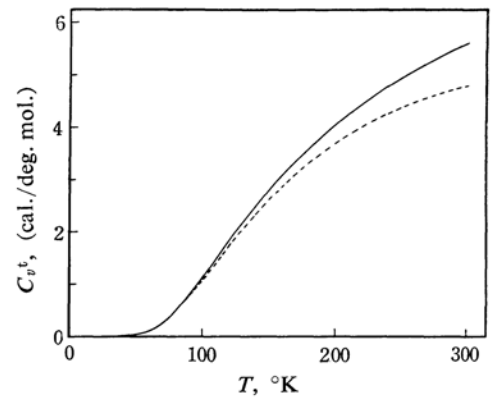

Fig. 11. Contribution from torsional oscillation to heat capacity.
——: $f(n, U_0, T)$, $n=4$, $U_0=4.00$ kcal./mol.
----: $E(\Theta_E/T)$, $\Theta_E=490$°K, $\nu=340\ cm^{-1}$

Finally, the "translational" or "lattice" heat capacity is computed by using this equation:

$$C_v^L=C_v(V_0)-f(n, U_0, T) \tag{15}$$

24) For instance, assuming $S=1$ and $U_1=kT_C$ for phase IV, we get a value of U_0 several per cent smaller than 4.00 ±0.16 kcal./mol.

25) F. Simon, *Ann. Phys.*, **68**, 241 (1922).

Figure 8 shows the temperature dependence of the Debye characteristic temperatures, $\Theta_D(V_O)$ and ${}_6\Theta_D(V_O)$, which correspond to the heat capacities C_v^L and $C_v^L+C_v^t$ respectively.

Phase Transition.—As is well known, neutron diffraction studies,[2] and theoretical consideration[26] of the anomalous changes of the heat capacities, and also of various other physical quantities at the gradual phase transition point (λ-point) (235°K for the bromide and 243°K for the chloride), have confirmed that the transitions are of the order-disorder type with relation to the orientations of the NH_4^+ ions in the crystalline lattice. If the orientations of the NH_4^+ ions are fully disordered above the λ-point and are completely ordered below it, the treatment of the Bragg-Williams type by Nagamiya[26] requires $R\ln 2$ e.u. as the entropy of transition.

In the case of ammonium chloride, the crystal structure in phase III is of the ordered CsCl-type and that of phase II, of the disordered CsCl-type. Moreover, the volume change at the transition point is very small. Thus the observed transition entropy may be only the contribution from a co-operative phenomenon arising from the order-disorder nature. The observed value, $\Delta S_{tr}=1.2$ e.u.,[27] is nearly equal to $R\ln 2$, which thus confirming the validity of the interpretation.

In the case of ammonium bromide, however, the crystal structures below and above the λ-transition point are slightly different from each other. The observed entropy change consists of the contributions from the order-disorder phenomenon and from the difference between the lattice energies of the two modifications. Staveley[28] estimated the entropy change of 0.34 e.u. for ammonium bromide by using Simon's heat capacity data.[1] However, as has already been mentioned, this value is not very reliable. The entropy change obtained in our measurements is 0.714 e.u., which is still much less than $R\ln 2$. To interpret this feature in ammonium bromide, we may take into account the fact that the orientations of NH_4^+ ions in phase III are already disordered by a considerable amount far below the λ-point; we also have a lower temperature modification (phase IV) in the case of this substance, while in ammonium chloride there is no such intermediate state.

On the other hand, the phase transition at 107.5°K is very likely of the first-order type, in view of the wide hysteresis[29] phenomenon and the slow establishment of thermal equilibrium near the transition point.

Summary

We have measured the heat capacities of the ammonium bromide crystal from 13°K to 305°K and have found two phase transitions in this temperature region. From the results, the heat and entropy of transitions at the transition points, 107.5°K and 235.0°K, have been derived: for the lower transition, $\Delta H_{tr}=29.29$ cal. mol.$^{-1}$ and $\Delta S_{tr}=0.271$ cal. deg^{-1} mol^{-1}; for the upper one, $\Delta H_{tr}=156.1$ cal. mol^{-1} and $\Delta S_{tr}=0.714$ cal. deg^{-1} mol^{-1}. The values of the entropy and enthalpy function at 298.15°K are: $S^\circ=26.97$ cal. deg^{-1} mol^{-1} and $(H^\circ-H_0^\circ)/T=13.56$ cal. deg^{-1} mol^{-1}. The torsional motions of the ammonium ions may well be represented in terms of a periodic potential function at the lowest temperature modification. The torsional frequency, 340 ± 7 cm^{-1}, and the potential barrier height, 4.00 ± 0.16 kcal. mol^{-1}, as determined on the basis of the thermal data, agree well with the values obtained in other experiments.

The infrared spectra of thin, non-scattering films of ammonium bromide have been obtained at 298°K, 100°K, 88°K, 40°K and 18°K. The torsional frequencies determined from the spectra by adopting Wagner-Hornig's assignments have been found to be almost independent of the temperature in the lowest modification.

The authors would like to express their sincere thanks to Dr. Takeshi Okuno of the Institute of Scientific and Industrial Research, Osaka University, who kindly permitted them to use and modify his cryostat for their spectroscopic measurement. The authors are also grateful to the members of their laboratory for their useful discussions.

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Note Added in Proof

(i) In order to interpret the small but significant difference between the torsional frequencies determined from infrared and Raman spectra, we measured the far-infrared spectra of ammonium bromide at about 100°K (phase III) and at room temperature (phase II) after the completion of

26) T. Nagamiya, *Proc. Phys. Math. Soc. Japan*, **24**, 137 (1942); **25**, 540 (1943).
27) C. C. Stephenson, R. W. Blue and J. W. Stout, *J. Chem. Phys.*, **20**, 1046 (1952).
28) L. A. K. Staveley, *Quart. Rev.*, **3**, 65 (1949).
29) Stephenson et al. found that this transition takes place at 108.5°K on heating and 78°K on cooling. We also reconfirmed the fact by differential thermal analysis.

this work. For the measurement a film of ammonium bromide on polyethylene plate was used. The spectra at 100°K show two peaks reproducibly; one is a considerably intensive peak at 345 cm^{-1} and the other is a weak one at 335 cm^{-1}. These two peaks, however, vanish at room temperature. From these facts, two peaks might be concerned with the active fundamental torsional frequency predicted by Wagner and Hornig.[8]

The authors would like to express their grateful acknowledgment to Dr. Tatsuo Miyazawa of the Institute for Protein Research, Osaka University, who permitted them to use Perkin Elmer Spectrometer (model 201 C) in his laboratory and gave them helpful advice.

(ii) Stephenson, Wulff and Lundell[30] reported quite recently the torsional frequencies of ammonium halide crystals determined from thermal analysis. For the torsional frequency in ammonium bromide they have quoted the Ph.D. thesis by A. G. Cole.[31] The heat capacity of ammonium bromide by Dr. Cole is about one per cent smaller than ours in the whole temperature region. With respect to the torsional frequency, however, the value, 335 ± 5 cm^{-1}, reported in Dr. Cole's thesis agrees rather well the result by us, $340+7$ cm^{-1}, within their experimental errors. In passing, we should like to remark that his value of the entropy of transition at 234.5°K is overestimated due to the no subtraction of the normal heat capacities from the total observed values. The authors are indebted to Microreproduction Laboratory of Massachusetts Institute of Technology for sending them the microfilm of Dr. Cole's thesis.

30) C. C. Stephenson, C. A. Wulff and O. R. Lundell, *J. Chem. Phys.*, **40**, 967 (1964).

31) A. G. Cole, Ph. D. Thesis, M. I. T. (1952).