

Low Temperature Specific Heats: III. Molecular Rotation in Crystalline Primary Normal Amyl Ammonium Chloride

J. C. Southard, R. T. Milner, and S. B. Hendricks

Citation: *The Journal of Chemical Physics* **1**, 95 (1933); doi: 10.1063/1.1749225

View online: <http://dx.doi.org/10.1063/1.1749225>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/1/1?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Low-temperature excess specific heat and fragility in polymers: Crystallinity dependence](#)

J. Chem. Phys. **109**, 7625 (1998); 10.1063/1.477384

[Low Temperature Specific Heat of Finely Divided Sodium Chloride](#)

J. Chem. Phys. **42**, 1112 (1965); 10.1063/1.1696048

[Low Temperature Specific Heats of Vitreous and Crystalline Silica](#)

J. Chem. Phys. **23**, 597 (1955); 10.1063/1.1742050

[The Specific Heat of Crystalline Selenium at Low Temperatures](#)

J. Chem. Phys. **21**, 1144 (1953); 10.1063/1.1699152

[Raman Spectrum of Crystalline Ammonium Chloride](#)

J. Chem. Phys. **4**, 88 (1936); 10.1063/1.1749805



Low Temperature Specific Heats: III. Molecular Rotation in Crystalline Primary Normal Amyl Ammonium Chloride*

J. C. SOUTHARD, R. T. MILNER AND S. B. HENDRICKS,† *Fertilizer and Fixed Nitrogen Division of the Bureau of Chemistry and Soils, and the Bureau of Standards*

(Received November 11, 1932)

The heat capacity of primary normal amyl ammonium chloride was measured between 20° and 280°K. If the substance is quenched to 90°K a metastable form is obtained which upon heating above 165°K slowly changes toward an apparently stable form. Two regions of gradual transition

were found. X-ray powder diffraction photographs taken above and below the transition regions were remarkably similar. The experimental results are interpreted on the basis of rotation of the $\text{NH}_3\text{C}_5\text{H}_{11}^+$ groups in the crystals.

L. PAULING¹ in his original work on the rotational motion of molecules in crystals considered the entropy of crystalline hydrogen and showed that the para molecules are rotating freely, even in the lowest state. He derived criteria for such motion and suggested that the gradual transitions shown by many solids accompany its excitation. The variations with temperature of some properties of crystalline sodium,² ammonium³ and potassium nitrates⁴ can be explained as arising from rotation of the nitrate groups.

Pauling suggested that the gradual transitions shown by HBr, HI, and the ammonium halides, and the transitions in solid N_2 , O_2 , and HCl accompany the excitation of molecular rotation. The abnormal increase in the dielectric constant of HCl⁵ at its transition point and the accurate

hexagonal close packed structure of solid nitrogen above 35.4°K⁶ support such an explanation. It also is probable that the molecules are rotating in solid CO, C_2H_6 , and CH_4 near their melting points. The high crystallographic symmetry of a number of ammoniates and hydrates at room temperature suggest that under such conditions the NH_3 and H_2O groups are spherically symmetrical.

In a number of other substances abnormal properties have been assumed to be caused by molecular rotation. Among these might be mentioned KCN,⁷ $\text{C}_{21}\text{H}_{44}$, $\text{C}_{23}\text{H}_{48}$, $\text{C}_{24}\text{H}_{50} \cdots \text{C}_{31}\text{H}_{64}$, $\text{C}_{34}\text{H}_{70}$,⁸ $\text{C}_{12}\text{H}_{25}\text{OH}$, $\text{C}_{18}\text{H}_{37}\text{NH}_3\text{Cl}$ ⁹ SiO_2 ,¹⁰ $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$,¹¹ and Na_2CO_3 .

There apparently are but few cases in which the structural peculiarities of the crystals so determine the potential function as to permit rotation of groups with relatively large moments of inertia which would lead to detectable alteration of x-ray diffraction patterns. An illustration is afforded, however, by certain substituted ammonium salts. An exemplar is primary n-amyl ammonium chloride,¹² $\text{NH}_3\text{C}_5\text{H}_{11}\text{Cl}$, the x-ray dif-

* This is one of a series of five joint publications, the others of which will appear later in the Journal of the American Chemical Society. The calorimetric determinations were made in the Cryogenic Laboratory of the Bureau of Standards and the x-ray measurements in the Fertilizer and Fixed Nitrogen Division of the Bureau of Chemistry and Soils.

† We are indebted to Dr. F. G. Brickwedde for laboratory facilities; to Mr. J. W. Cook for the liquefaction of the hydrogen, to Mr. M. E. Jefferson and Mr. V. L. Mosley for assistance in the x-ray work, and to Mr. E. F. Jansen for purification of the amines used.

¹ L. Pauling, *Phys. Rev.* **36**, 430 (1930).

² F. C. Kracek, E. Posnjak and S. B. Hendricks, *J. Am. Chem. Soc.* **53**, 3339 (1931).

³ S. B. Hendricks, E. Posnjak and F. C. Kracek, *J. Am. Chem. Soc.* **54**, 2766 (1932).

⁴ T. Barth and F. C. Kracek, *Phys. Rev.* **40**, 1034 (1932).

⁵ R. M. Cone, G. H. Denison and J. D. Kemp, *J. Am. Chem. Soc.* **53**, 1278 (1931).

⁶ M. Ruhemann, *Zeits. f. Physik* **76**, 368 (1932).

⁷ R. W. G. Wyckoff, *The Structure of Crystals*, New York, 1931, p. 364.

⁸ A. Muller, *Nature* **129**, 436 (1932).

⁹ J. D. Bernal, *Nature* **129**, 870 (1932).

¹⁰ J. D. Bernal and W. A. Wooster, *Annual Reports of the Chemical Society, Crystallography*, London, 1931, p. 291.

¹¹ F. C. Kracek, S. B. Hendricks and E. Posnjak, *Nature* **128**, 410 (1931).

¹² S. B. Hendricks, *Zeits. f. Krist.* **74**, 29 (1930); *Nature* **126**, 167 (1930).

fraction characteristics of which have been thoroughly studied at room temperature and in which the rotating groups have sufficient scattering power to influence the intensities of x-ray reflection. The result of heat capacity determinations and x-ray diffraction photographs at various temperatures for this substance are described below.

PREPARATION OF MATERIAL

The amine as purchased from the Eastman Company was first distilled from NaOH, and then from CaO. It was then twice fractionally distilled. The final material boiled between 104.6–105° (corrected, 747.4 mm).

The amine was dissolved in pure absolute diethyl ether and to it was added a solution of dry HCl in absolute ether. The precipitated salt was removed by filtration and washed repeatedly with dry ether. It was dried at 75° for several hours and then allowed to stand over CaCl₂ for some months before it was introduced into the calorimeter.

HEAT CAPACITY MEASUREMENTS

The heat capacity measurements were made with an adiabatic calorimeter described elsewhere.¹³ The complex behavior of the compound entailed many unanticipated experiments.

If primary n-amyl ammonium chloride is cooled rapidly to below 165°K and then subjected to C_p measurements below that temperature, reproducible values are obtained. Such a quenched form when heated to about 175°K, spontaneously evolves heat at a sufficiently high rate to warm the calorimeter 0.1° per minute (maximum). Reproducible C_p measurements could not be made in the region between 165°K–230°K, but approximate measurements indicate no transition up to about 210°K. Between 210 and 230° the compound undergoes a gradual transition. The total amount of heat absorbed between 165 and 230°K is apparently a reproducible quantity since two measurements agreed to within 0.03 percent. From 230 to 242°K the heat capacity values were apparently quite normal and reproducible. Between 242 and 252°K a second gradual transition took place. Repro-

TABLE I. *Heats of transition of n-amyl ammonium chloride.*

Quenched form	Run I cal./mole	Run II cal./mole
$H_{242.90} - H_{154.92}$ (measured; max. C_p at $221.5 \pm 0.5^\circ\text{K}$)	3944.1	3945.3
Estimated heat of transition	282.6	283.8
$H_{256.94} - H_{242.90}$ (measured; max. C_p at $246.5 \pm 0.5^\circ\text{K}$)	710.7	710.7
Estimated heat of transition	32.1	32.1
Annealed form		
$H_{229.21} - H_{199.37}$ (measured; max. C_p at $222.0 \pm 0.5^\circ\text{K}$)	1474.0 cal./mole	
Estimated heat of transition	215.4	
$H_{254.61} - H_{229.21}$ (measured; max. C_p at $246.5 \pm 1.0^\circ\text{K}$)	1811.8	
Estimated heat of transition	568.2	

ducible measurements of the energy of the transition, which was much smaller than that of the lower transition, could be made. The various energy values measured are listed in Table I, as are also the heats of transitions estimated by subtracting the graphically interpolated normal heats which presumably would have been observed had there been no transitions.

If primary n-amyl ammonium chloride was allowed to stand at *ca.* 195°K for a number of days a second, apparently stable, modification was obtained. The results of a number of C_p measurements made on successive days are plotted as Fig. 1. A steady state upon which reproducible measurements could be made was slowly approached. This annealed form was used for C_p

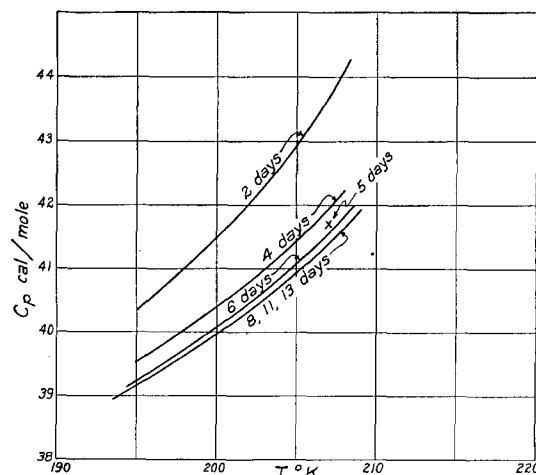


FIG. 1. The heat capacity of n-amyl ammonium chloride after annealing at 195°K for various times.

¹³ J. C. Southard and F. G. Brickwedde. To be published.

measurements from 14°K to above the ice point. It also showed two gradual transitions in the same regions as the quenched form; their magnitudes, however, were entirely different (Table I). Above 257°K the two forms had the same heat capacity.

Two attempts were made to regain the form upon which extensive measurements had been carried out by allowing the compound to stand at 195°K as before, in one instance for more than a month. The heat capacity curves obtained from these annealed forms were similar to that of the annealed form described above, but were not coincident with it. In one instance the values were somewhat low, in the other slightly high. In all these cases no change in C_p values with time were detected once a stable state had been reached.

In one experiment primary n-amyl ammonium chloride was cooled from room temperature to 230°K which is below the second transition but above the first. Heat capacity measurements were then made without evidence of the transition. The data indicate that there are at least three forms of primary n-amyl ammonium chloride. These are designated as *A*, *B*, and *C*, *C* being the

form stable at room temperature. If it is assumed that the lower transition is characteristic of a change from a metastable form *A* to *C*, and the higher transition of some form, *B* to *C*, then it follows that all the measurements below 230°K were made on mixtures of *A* and *B*. The composition of the mixtures can be estimated from the heats of transition. On such a basis the quenched form contained 1.4 percent *B*, the annealed 25 percent *B*.

Heat capacity measurements on the quenched and annealed forms are listed in Table II and the transitions shown in Fig. 2. Since the heat capacity values of the two samples are the same above 257°K, it may be assumed that the compound has in each instance returned to the same form. If this form is taken as a standard state the differences in entropy between the two samples at low temperatures can be calculated from their heat capacities and transition energies. Such a calculation shows that at 20°K the difference in molal entropy between quenched and annealed forms is 0.15 E.U. This value possesses no significance since it is within experimental error. The

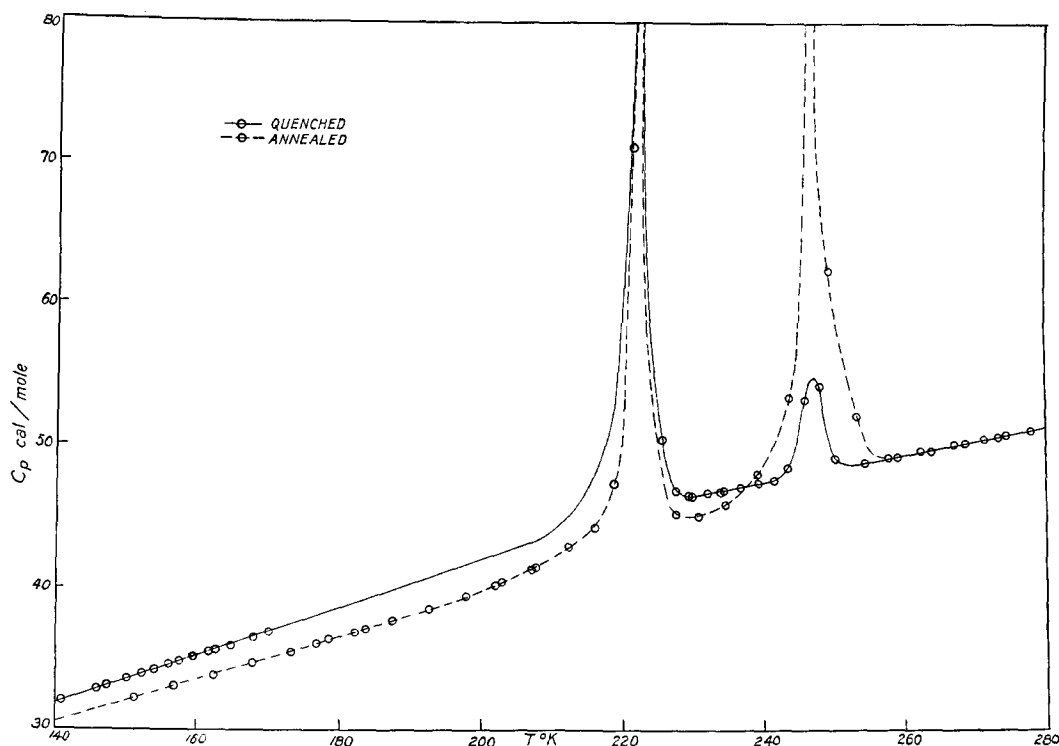


FIG. 2. Molal heat capacity of n-amyl ammonium chloride.

molal entropy of primary n-amyl ammonium chloride at 298.16°K is 63.74 E.U. as shown in Table III.

X-RAY DIFFRACTION CHARACTERISTICS

X-ray powder diffraction photographs of primary n-amyl ammonium chloride were made

TABLE II. *Molal heat capacity of n-amyl ammonium chloride.*

Mol. wt. 123.58.		Weight of sample (in vacuo) 29.646 g 273.16°K = 0°C	
Quenched			
T°K	C_p cal./mole deg.	T°K	C_p cal./mole deg.
July 2, 1931		July 22, 1931 (cont.)	
Liq. air bath		Liq. H ₂ bath	
97.09	23.89	81.35	20.49
101.04	24.65	85.35	21.52
104.90	25.43	89.56	22.41
108.68	26.17	141.31	32.06
112.39	26.91	150.45	33.64
116.34	27.57	156.21	34.61
120.54	28.47	161.90	35.53
124.65	29.03	Nov. 17, 1931	
128.70	29.89	Liq. air bath	
132.69	30.48	147.66	33.14
July 8, 1931		152.51	33.95
Liq. air bath		157.62	34.81
125.94	29.29	162.82	35.64
129.98	30.08	168.02	36.49
133.95	30.79	225.65	50.39
137.88	31.42	227.70	46.80
146.37	32.85	229.83	46.44
150.70	33.65	232.09	46.65
154.98	34.36	234.47	46.86
159.23	35.06	236.86	47.04
July 20, 1931		239.37	47.39
Liq. air in vac.		241.71	47.53
66.20	17.46	243.58	48.49
70.80	18.11	245.85	53.33
75.09	19.01	248.02	54.30
79.20	19.98	250.26	49.11
83.51	21.08	252.60	49.14
88.03	22.13	254.96	48.93
92.38	22.95	257.34	49.08
96.62	23.80	259.72	49.25
100.75	24.59	262.09	49.45
104.77	25.41	Nov. 28, 1931	
113.53	27.27	Liq. air bath	
117.93	27.87	154.25	34.25
122.26	28.68	159.64	35.15
July 22, 1931		164.97	35.91
Liq. H ₂ bath		170.23	36.92
22.34	4.36	CO ₂ acetone bath	
26.21	5.53	229.48	46.53
30.60	7.00	234.00	46.79
35.44	8.50	238.51	47.20
40.64	10.05	254.58	48.79
46.64	11.70	259.31	49.16
52.68	13.41	264.04	49.58
58.20	14.96	268.76	50.14
63.37	16.25	273.48	50.61
68.24	17.39	278.19	51.00
72.84	18.42		
77.19	19.47		

TABLE II. (Continued).

Annealed			
T°K	C_p cal./mole deg.	T°K	C_p cal./mole deg.
Nov. 2, 1931		Nov. 9, 1931 (cont.)	
Liq. air bath		Liq. H ₂ bath	
176.98	36.04	39.64	9.59
182.28	36.85	45.26	11.30
187.53	37.71	50.80	12.69
192.73	38.55	55.85	14.21
197.87	39.46	60.59	15.35
202.95	40.52	65.09	16.39
Nov. 5, 1931		66.07	16.64
CO ₂ acetone bath		70.27	17.54
202.50	40.42	74.48	18.53
207.77	41.54	78.71	19.42
Nov. 6, 1931		82.76	20.44
Liq. air bath		87.05	21.34
103.51	24.48	91.56	22.23
110.00	25.58	96.29	23.14
116.31	26.54	101.24	24.05
122.45	27.91	Nov. 11, 1931	
128.45	28.56	CO ₂ acetone bath	
134.35	29.55	202.00	40.27
140.15	30.41	207.24	41.33
145.86	31.33	212.39	42.91
151.49	32.22	216.19	44.24
157.04	33.07	218.88	47.36
162.54	33.81	221.35	71.16
167.98	34.71	227.70	45.14
173.35	35.45	230.73	45.09
178.66	36.39	234.62	45.96
183.92	37.09	239.29	47.99
Nov. 9, 1931		243.72	53.44
Liq. H ₂ bath		249.33	62.42
15.57	2.12	253.41	52.13
18.38	2.96	257.92	49.11
21.97	4.06	262.55	49.62
26.18	5.40	267.17	50.09
30.62	6.85	271.32	50.51
34.96	8.19	274.54	50.74

under various conditions suggested by the heat capacity work. It would have been far more desirable in the case of such a complex compound to make observations on single crystals but at low temperatures the technique for doing this would be somewhat involved and preliminary observations indicated that it would be difficult or impossible to prevent destruction of the crystals upon cooling. The perfect basal cleavage and micaceous character of the compound made it extremely difficult to obtain powder photographs free from effects due to crystal orientation.

The final type of diffraction camera used and the method of cooling the sample are shown in Fig. 3. In this apparatus the film is external to the vacuum system and can be changed without disturbing the sample. The sample, as shown by measurement does not differ in temperature from the cooling medium by as much as 5°. Its condi-

tion is readily observable at any moment. The camera radius was made about 10 cm in order to enhance the accuracy of the measurements.

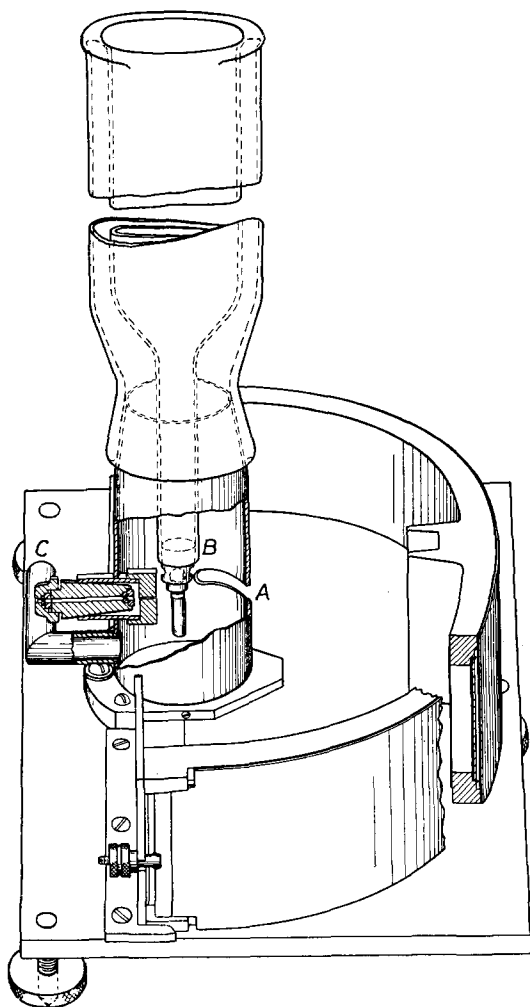


FIG. 3. X-ray powder diffraction camera for low temperatures with film external to the vacuum system; A, 5 mm slot covered with cellophane; B, copper to glass seal; C, tube leading to vacuum system.

Data from powder photographs of primary *n*-amyl ammonium chloride obtained under the following conditions are listed in Table IV. (1) Room temperature (298°K); (2) Liquid air temperatures (90°K); (3) Solid CO₂ temperature (195°K) after being heated from liquid air temperature; (4) Then allowed to stand for three days at solid CO₂ temperatures and photographed (195°K); (5) After the completion of (4) cooled to liquid air temperatures (90°K).

The same sample was used throughout this group of exposures. The lattice dimensions under these various conditions are:

- (1) $a = b = 5.00\text{\AA}$, $c = 16.70\text{\AA}$, $2\text{C}_5\text{H}_{11}\text{NH}_3\text{Cl}$ in unit
- (2) $a = b = 6.81$, $c = 16.70$, $4\text{C}_5\text{H}_{11}\text{NH}_3\text{Cl}$
- (3) $a = b = 6.97$, $c = 16.70$, $4\text{C}_5\text{H}_{11}\text{NH}_3\text{Cl}$
- (4) $a = b = 7.06$, $c = 16.70$, $4\text{C}_5\text{H}_{11}\text{NH}_3\text{Cl}$
- (5) $a = b = 6.87$, $c = 16.70$, $4\text{C}_5\text{H}_{11}\text{NH}_3\text{Cl}$.

It was assumed, as the standard for the measurements, that the lattice dimensions at 298°K are as listed above. These had previously been obtained from measurements on single crystals.

A number of untoward effects were evident on these photographs. It was practically impossible to obtain at 298°K a sample free from crystal orientation as shown by equality of intensities throughout the diffraction cones. This persisted upon cooling to 90°K and was accompanied by

TABLE III. Entropy of *n*-amyl ammonium chloride

0° to 20°K (extrapolated entropy)	1.28
20° to 298.16°K (measured entropy, disregarding transitions)	61.05
First transition 283.2/221.5	1.28
Second " 32.1/246.5	.13
Total	63.74 E.U.

broadening of the diffraction maxima, which caused difficulty in detecting weak intensities. At 195°K, however, the orientation and the broadening were not observable. At the end of four days standing at 195°K the particle size had markedly increased. The only variable other than time was the slow accumulation of H₂O resulting from a minute leak in the system (the pressure was of the order of 10⁻⁵ mm of Hg).

The change at 195°K upon standing is accompanied by an expansion of the lattice. In evaluating other changes a number of possible sources of error must be borne in mind. Possible impurities in the samples are H₂O, Hg, and CO₂. The Cu $K\alpha$ radiation contained some Cu $K\beta$ and Ni $K\alpha_1$, the latter from the base of a barium promoted Cu filament, the Cu being plated on Ni. At 195°K, before long standing, the presence, with moderate intensity of (210) was noted. This reflection could not be explained on the basis of a unit of

TABLE IV. Powder photographic data from primary amyl ammonium chloride, Cu K α_1 radiation (radius, 10.08 cm).

Room temperature		Liquid air temperature. Sample cooled quickly		Solid CO ₂ temperature. warmed from liquid air temperature		After standing for three days at solid CO ₂ temperatures		Liquid air temperature after standing for four days at solid CO ₂ temperature			
$\sin^2 \theta = 0.02359(h^2 + k^2) + 0.000212j^2$ $a = b = 5.003(7.074) \quad c = 16.70$		$\sin^2 \theta = 0.01272(h^2 + k^2) + 0.000214j^2$ $a = b = 6.813 \quad c = 16.70$		$\sin^2 \theta = 0.01214(h^2 + k^2) + 0.000214j^2$ $a = b = 6.974 \quad c = 16.70$		$\sin^2 \theta = 0.01185(h^2 + k^2) + 0.000214j^2$ $a = b = 7.064 \quad c = 16.70$		$\sin^2 \theta = 0.01250(h^2 + k^2) + 0.000214j^2$ $a = b = 6.874 \quad c = 16.70$			
Plane	$\sin^2 \theta$ calc.	$\sin^2 \theta$ obs.	Plane	$\sin^2 \theta$ calc.	$\sin^2 \theta$ obs.	Plane	$\sin^2 \theta$ calc.	$\sin^2 \theta$ obs.	Plane	$\sin^2 \theta$ calc.	$\sin^2 \theta$ obs.
(101) β	0.02100	0.02065	(111) β	0.02254	0.02226	(111) β	0.02160	0.02152	(111) β	0.02714	0.02647
(101)	.02572	.02572	(111)	.02759	.02726	(111)	.02642	.02647	(111)	Ni K α_1	.03140
(102)	.03209	.03207	(112)	.03401	.03393	(111)Ni K α_1	.03056	.03066	(112)	Ni K α_1	.03356
(004)	.03402	.03403	(113)	.04471	.04477	(112)	.03284	.03280	(113)		.04426
(110) β	.03854	.03818	(200)	.05090	.05098	(004)	.03531	.03524	(200)		.05000
(113) β	.04027	.04020	(201)	.05304	.05317	(200) β	.03965	.03964	(201)		.05214
(103)	.04272	.04289	(220)	.10180	.10086	(201) β	.04142	.04088	(201)	Ni K α_1	.05786
(110)	.04718	.04687				(113)	.04354	.04277	(201)Ni K α_1	.06030	.06002
(111)	.04930	.04933				(200)	.04856	.04858			
(114)	.08119	.08162				(201)	.05070	.05085			
						(200)Ni K α_1	.05640	.05702			
						(201)	.05880				
						(210)	.06070	.06080			
						(203)	.06782	.06729			
						(220)	.09712	.09712			
						(221)	.09926	.09910			

Intensity differences, previously reported, in diffraction patterns made under various conditions, are hardly trustworthy. Although there are apparently some true differences they are not considered of sufficient accuracy to emphasize.

DISCUSSION

n-Amyl ammonium chloride has properties similar to both ionic and molecular compounds. A number of structural peculiarities are perhaps evident from an examination of the apparent unit of structure (base *ABCD*) and atomic arrangement shown in Fig. 5a. The value of α is but slightly greater than the corresponding value for the high temperature modification of ammonium chloride. (Compare Figs. 5a and b.) In fact the structure can be considered as made up of ionic layers simulating the "high" ammonium chloride arrangement separated by groups of two

¹⁴ G. Shearer, Proc. Roy. Soc. (London) **A108**, 655 (1925); A. Muller, *ibid.* **A120**, 437 (1928).

molecular layers of long hydrocarbon groups parallel to the tetragonal axis; the two molecular layers being separated by a displacement along it in a manner such that they apparently do not interleave. This too is indicated by an increase of *ca.* 2.10Å in the value of c_0 for each added methylene group in the homologous series. The area normal to the tetragonal axis occupied by a hydrocarbon group is 25.0Å² which is markedly

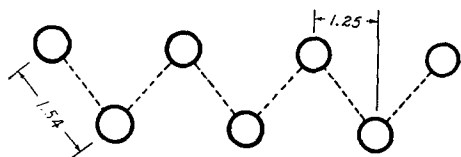


FIG. 4. Probable arrangement of carbon atoms in a saturated hydrocarbon molecule.

greater than the average value 18.0Å² found for many fatty acids and strictly molecular organic compounds¹⁵ but decidedly smaller than twice this value. This structural peculiarity apparently necessitated by the ionic nature of the compound might well be a factor in so determining the value of the potential function as to permit molecular rotation at room temperatures.

If crystals of primary n-amyl ammonium chloride are cooled to a sufficiently low temperature the rotation of the $C_5H_{11}NH_3^+$ groups must stop. In the equilibrium condition the various atoms would occupy positions required by the crystal symmetry. The diffraction pattern of such a material would, in the absence of polymorphic changes, be similar to that obtained at room temperature. There would, however, be some differences; notably, a change in the crystal symmetry and the appearance of reflections from planes requiring a larger unit of structure and possibly from (*hko*) with (*h+k*) odd. The most striking characteristic of the diffraction patterns obtained from primary n-amyl ammonium chloride under various conditions is their close similarity. A reflection requiring a larger unit of structure is present on photographs at 195°K and probably on poorer photographs at 90°K.

The x-ray diffraction patterns afford no very conclusive answer to the question of the nature of the various unstable forms of primary n-amyl ammonium chloride encountered in the heat

capacity measurements. An explanation consistent with the unusual behavior of this compound is suggested below.

In crystalline n-amyl ammonium chloride at 300°K the $NH_3C_5H_{11}^+$ groups are rotating about the tetragonal axis with an approach to constant angular velocity. If the compound is quickly cooled to some temperature below 165°K, the molecules are stopped in certain positions that are not the equilibrium ones. At such a temperature the rate of approach to the equilibrium state is very slow. However, if the compound is heated above 165°K some of the molecules have sufficient freedom to move into more stable positions with a corresponding evolution of energy. If the temperature is further raised to 195°K the rate of evolution of energy decreases markedly with time and finally it is possible to carry out adiabatic measurements of the heat capacity. The change to the stable configuration continues, however, and if a sufficient period of time has elapsed a heat capacity markedly lower than that of the quenched form is obtained.

The $C_5H_{11}NH_3^+$ groups apparently are not rotating in either the quenched or the partially annealed forms. If the temperature of either form is raised a region of gradual transition in which

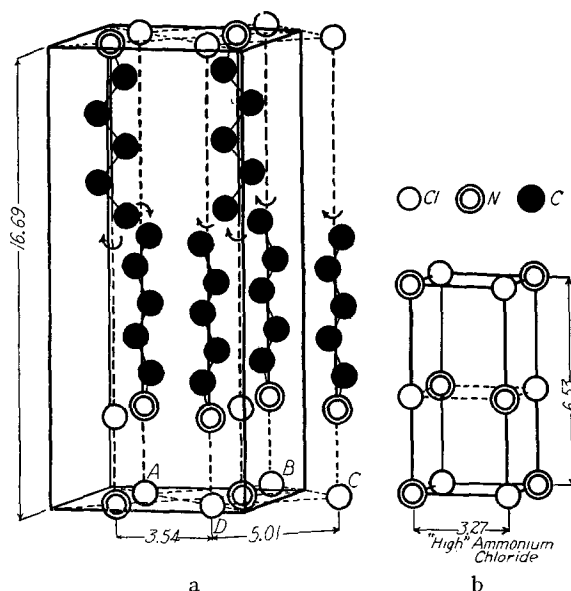


FIG. 5a. The atomic arrangement in n-amyl ammonium chloride.

FIG. 5b. A portion of the unit of structure of high ammonium chloride.

¹⁵ A. Muller, Proc. Roy. Soc. (London) **A114**, 542 (1927).

molecular rotation sets in is reached. These temperatures are not the same for the two forms, indeed it is probable that that of the more stable form will be the higher. In practice, however, it is not possible to obtain what one might call the pure quenched or annealed forms. Thus it is expected that the various materials would show two transitions, the magnitudes of which would depend upon the time of annealing.

The presence of two transitions further suggests that the quenched and annealed forms partially exist in separate phases. If the quenched form is allowed to stand the molecules in a small crystal will slowly go into their equilibrium positions. When a sufficiently great number have

changed the lattice as a whole becomes dynamically unstable and then quickly changes to the stable form. It is probable that few crystals of the stable form were present in the samples used for the x-ray diffraction photographs.

It might be pointed out that the case of *n*-amyl ammonium chloride is similar in principle to that of NO^{16} (or N_2O_2) and CO .¹⁷ In these cases it has been suggested that there is within the lattice a lack of discrimination in quenched forms between the stable positions of the molecules and ones differing from them by 180° rotation.

¹⁶ H. L. Johnston and W. F. Giauque, *J. Am. Chem. Soc.* **51**, 3194 (1929).

¹⁷ J. O. Clayton and W. F. Giauque, *ibid.* **54**, 2610 (1932).