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Thermodynamic Properties of the Three Crystalline Forms of Methylammonium Chloride

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In methylammonium chloride it is usually assumed that the seat of the charge of the positive ion is close to the nitrogen atom. However, if there were sufficient polarization to move this charge close to the middle of the molecule it is conceivable that the two ends of the molecule might be sufficiently alike to cause random orientation in the crystal, producing a discrepancy between the actual entropy at room temperature and that determined by the third law of thermodynamics. This discrepancy could be detected by computing the free energy of the dissociation reaction

$$[CH_3NH_3^+]Cl^-(s) \longrightarrow CH_3NH_2(g) + HCl(g)$$

using the third law entropy of methylammonium chloride together with previously determined values of methylamine vapor and gaseous hydrogen chloride to obtain a value of ΔS and combining this with a calorimetric value ΔH. This calorimetric value of ΔF would differ from a value obtained from cell measurements by $RT \ln o$, where o is unity if there is no random orientation. Preliminary experiments indicate that cell measurements of this reaction can be made in ethyl alcohol as solvent using the hydrogen and silver–silver chloride electrodes.

Accordingly heat capacity measurements were made on methylammonium chloride down to temperatures attainable with liquid hydrogen.

Three distinct crystalline modifications (α, β and γ) were found, two of which (β and γ) could be cooled down to liquid hydrogen temperatures and were in equilibrium at 220°K. The same value of the entropy of the form stable above this transition (γ) was calculated from its low temperature heat capacities as was calculated from those of the β form together with the heat of transition to the γ form. Thus both the β and the γ forms have the same degree of randomness or there is no randomness in either. The first alternative is sufficiently improbable to indicate strongly the absence of randomness in the crystal of methylammonium chloride at low temperatures.

For this reason the cell measurements have been temporarily discontinued but the additional calorimetric data necessary to calculate the heat and free energy of the dissociation of the salt into gaseous hydrogen chloride and the gaseous amine are presented. They consist of measurements of the heat of neutralization of aqueous methylamine by aqueous hydrochloric acid as well as the heat of solution of liquid methylamine and solid methylammonium chloride in water at 25°.

Preparation and Purification of Methylamine and Methylammonium Chloride.—About 140 g. of pure ammonia free methylamine was prepared as previously described.[1]

A middle cut was distilled into aqueous hydrochloric acid and the resulting dry methylammonium chloride (m. p. 226) recrystallized from absolute alcohol. No change in melting point was observed on recrystallization. The salt was ground in an agate mortar after preliminary drying at 105°. The last traces of water were removed by drying under a vacuum between 10^{-4} and 10^{-6} mm. of mercury for thirty hours in a boiling water-bath, with shaking, until the pressure did not rise above 10^{-4} mm. after shutting the pump off for one hour.

When the 46-g. sample was transferred to the calorimeter for the low temperature heat capacity measurements, the relative humidity was less than 35%. The weight gained by the calorimeter was within one milligram of that lost by the flask containing the salt. This was the invariable procedure in transferring the dry salt.

The Density of Methylammonium Chloride.—For the purpose of making buoyancy corrections a rough determination of the density was made by the displacement of toluene, in which it was insoluble, using a picnometer. The results of separate determinations were 1.210 and 1.217 g./cc.

The Molal Heat Capacities of Methylammonium Chloride from 12 to 298°K.—The apparatus is shown in Fig. 1. It is similar to that described by Southard and Brickwedde.[2a,b] The calorimetric vessel (1) of 87 cc. capacity is made of copper with a 0.09 cm. wall and contains 179 g. of copper. Twelve radial vanes, 0.02 cm. thick, are soft-soldered to the inside wall of the calorimeter and to the thermometer well (2). The thermometer well (2) is a reentrant tube, 1.0 cm. o. d. with a 0.1 cm. wall, silver soldered to the bottom. The vessel carries a chamber of 5 cc. capacity, soft-soldered to the side of the calorimeter, the wall being curved to fit the calorimeter circumference. This chamber, intended for use as a vapor pressure thermometer, has short tubes connected to the top and bottom. In these measurements, however, both tubes were left open. The calorimeter is gold plated inside and out and closed by the cap (4) which carries a German-silver capillary for filling and for evacuation, and which fits into a trough (5) filled with Rose metal as a seal. The thermometer well contains two four-lead resistance thermometers (6) and (7), one of no. 38 B. and S. platinum-rhodium wire (R-201, ice-point resistance 80.6 ohms.) and the other of no. 40 B. and S. constantan wire (R-103, ice-point resistance 114 ohms.). Both are wrapped on the same mica cross which fits inside a platinum thimble, the leads being taken out through a soft glass cap (8). A current and a potential lead are common to both thermometers. Thus, there are three potential leads and three current leads.

The calorimeter heater (9) (resistance 81 ohms) of no. 40 B. and S. double silk insulated constantan wire was wound bifilarily on the half of the platinum case of the resistance thermometer nearest the cap after coating the latter with bakelite varnish. Two coats of bakelite varnish were applied and the whole baked at 110° for an hour. Care was taken to insulate the soldered connections to the three no. 36 B. and S. copper wires to which the leads from the shield were attached. These connections are located 5 mm. inside the well. The uncovered

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(1) Aston, Siller and Messerly, THIS JOURNAL, **59**, 1743 (1937).

(2) (a) Southard and Brickwedde, *ibid.*, **55**, 4378 (1933); (b) see also Aston and Eidinoff, *ibid.*, **61**, 1533 (1939).

end of the platinum thimble was tinned with Wood's metal and the entire assembly cast into the thermometer well with Wood's metal so that the junctions of the supply wire terminals to the heater were entirely covered.

The connections from shield to the heater consist of two current leads and one potential lead each of 10 cm. of no. 36 B. and S. D. S. copper wire. The other potential lead is tapped out from the corresponding current lead where it passes through the shield. In this way, the potential across half of the leads is measured thus eliminating the lead correction. The use and design of this heater was suggested by Dr. F. G. Brickwedde of the National Bureau of Standards. The connections from the resistance thermometer to the shield consist of three no. 36 B. and S. D. S. platinum wires for potential leads and three no. 36 B. and S. D. S. copper wires for current leads. The calorimeter hangs by three silk cords from the top of the adiabatic shield (10). There are difference thermocouples between the top and bottom and the side of the shield and between the calorimeter and the side of the shield. The junction of thermocouple S-1[3] is fastened to the side of the calorimeter. This thermocouple is wrapped around the outside of the shield for a distance of 35 cm. and passes through 10 cm. of 0.125 in. o. d. copper tube, filled with paraffin and soldered to the inside surface of the shield. It finally passes through the lead block discussed later in such a way that 72 cm. are taken up from the junction to where it leaves the block, thus making the temperature gradients the same as in the original calibration.[3] The supply wires to the resistance thermometers, the constantan heater and the difference thermocouples are wrapped around the shield in machined grooves to bring them to the temperature of the latter. These wires are 110 cm. long.

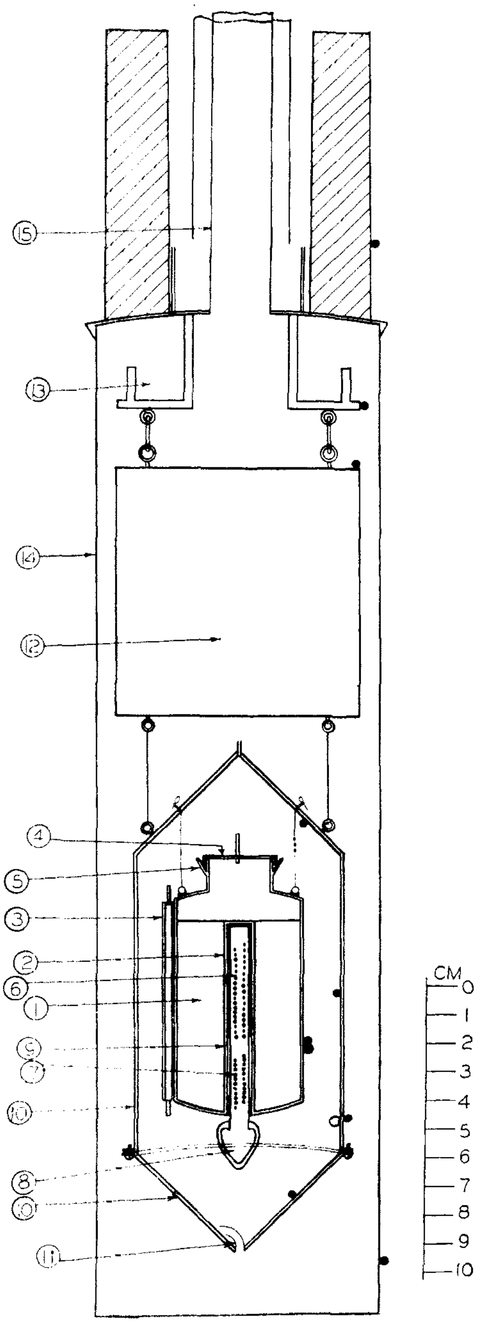

Fig. 1.—Calorimeter assembly: 1, calorimeter; 2, thermometer well; 3, vapor pressure chamber; 4, cap; 5, seal; 6, platinum–rhodium thermometer; 7, constantan thermometer; 8, "normal" glass cap; 9, constantan heater; 10, radiation shield; 11, evacuating tube; 12, lead block; 13, copper annular ring with wire fastened in by paraffin; 14, monel metal cryostat "can"; 15, monel tube; ●, thermocouple junctions.

Those for the resistance thermometer potential leads are of no. 36 B. and S. D. S. platinum wire while those for the current leads are of no. 28 B. and S. D. S. copper wire. The wires for the heater are no. 28 B. and S. D. S. copper while those for the difference couples are no. 30 B. and S. D. S. copper.

The top, bottom and sides of the shield are made of 0.11 cm. thick copper and are wrapped with no. 36 B. and S. D. S. constantan heaters, closely wound, fastened with bakelite laquer and covered with thin copper foil. The inside of all parts is gold plated. Provision for evacuation is made by the bent 0.125 inch o. d. copper tube. The shield is supported from the heavy lead block (12) by cords.

The purpose of this lead block (12) is to form a thermal dam for heat leaking down the wires. The platinum potential leads to the thermometers are connected to copper inside it. Wires are cast into this block with Woods metal after thoroughly impregnating their insulation with bakelite laquer and baking. The entering wires are soldered to the upper end and wires to the calorimeter system to the lower end. Three special wires consisting of an upper half of no. 36 B. and S. D. S. platinum and a lower half of no. 30 B. and S. D. S. copper with the joint insulated with cigarette papers and bakelite laquer are cast into this block with Woods metal. The upper (platinum) half of each is connected by platinum wire to the upper end of a no. 36 B. and S. D. S. platinum wire cast into the block, whose lower end is connected to the thermometer potential lead, while the lower (copper) half of each special wire is connected to the lower end of a no. 18 B. and S. Vitrolex covered copper wire also cast in the block whose upper end eventually passes to the potentiometer system. In this way it is made certain that the copper–platinum junctions are all at the temperature of the lead block. The rest of the wires passing through this block are no. 18 B. & S. Vitrolex covered. All the connections to the upper end of this lead block are wrapped twice around the annular trough or ring (13) and fastened to it with paraffin which fills the remainder of the annulus. Control thermocouples are located at the points marked in Fig. 1.

The monel can (14) is fastened to its cover with a soft solder joint and is evacuated through the central tube (15) which also carries the supply wires and serves to support this can inside a large dewar tube, $4^5/_{16}$ in. i. d. × $35^5/_{16}$ in. inside length (11 × 89 cm.). The rest of the apparatus and the operation of the calorimeter is as already described.[2b]

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(3) Aston, Willihnganz and Messerly, This Journal, 57, 1642 (1935).

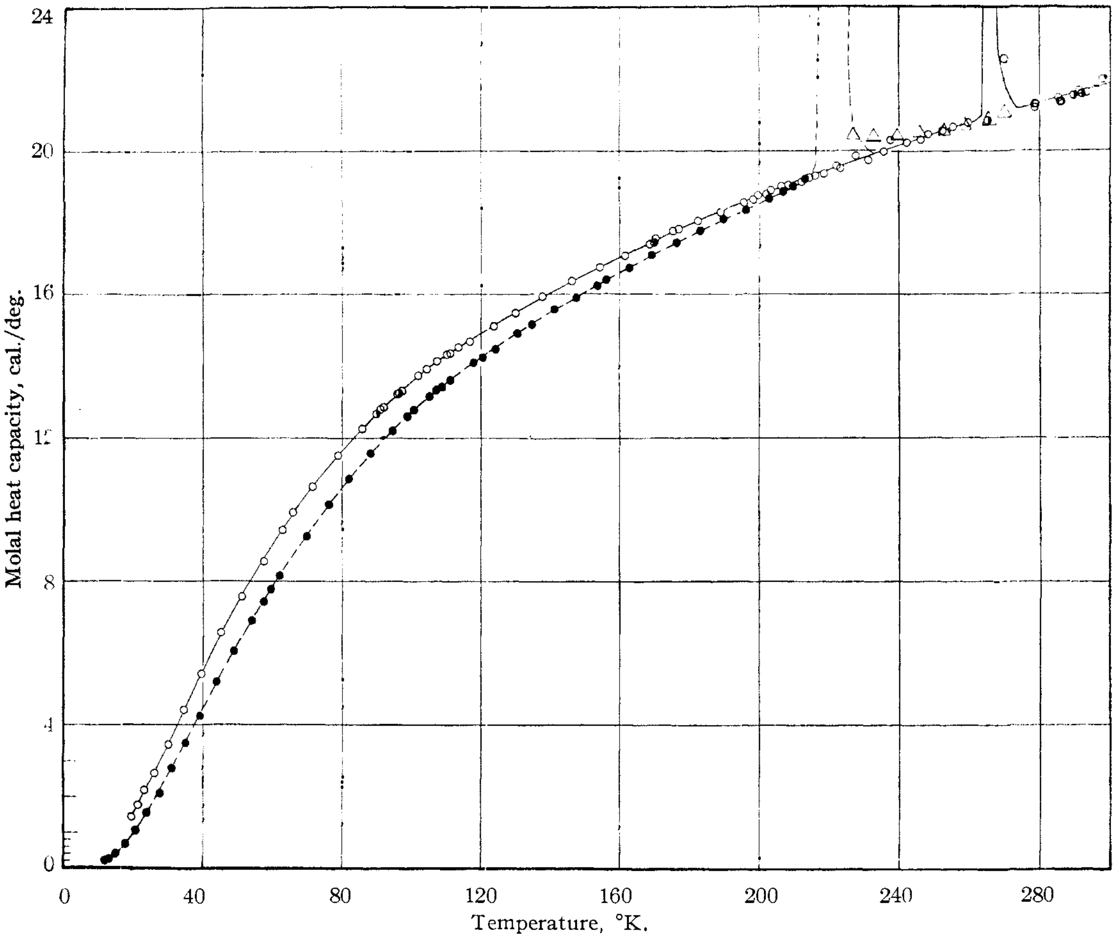

Fig. 2.—The molal heat capacity of methylammonium chloride: O, alpha form above 264.5°; ●, beta form; O, gamma form below 264.5°; Δ, supercooled alpha form; ◑, resistance thermometer used as heater.

After introducing the methylammonium chloride, the calorimeter was evacuated to better than 10^{-5} mm. of mercury and then helium admitted to produce a pressure of 40 mm. of mercury for the purpose of heat conduction. The small tube was then pinched shut where it had been tinned inside with solder and heated in this place to melt this solder. The rest of the tube was then cut off.

The heating periods were timed with a mechanical precision timer, constructed in this laboratory, but quite similar to that described by Johnston,[4] controlled by a Gaertner chronometer through a thyratron relay. The chronometer was frequently checked against the Arlington time signals through the courtesy of Western Union.

In heating the shield system, the shield heaters are connected in series. There is a 10,000 ohm variable resistance in parallel with the side and 5,000 ohm variable resistance in parallel with the bottom and top. These are used to compensate for slight differences in the heating rate.

After assembly it was found that the difference thermocouples between both the top and the bottom of the shield and the side were not functioning. It was calculated from the weights of the top, bottom and side of the shield and the heater resistances that 3000 ohms in parallel with the side would produce uniform heating. This method of heating the shield produced no drifts of the calorimeter, during the fore and after periods, when the difference couple between the calorimeter and the shield side, which always operated satisfactorily, indicated no temperature difference. After these measurements the difference couple between the bottom of the shield and the side was repaired. It was then found that this parallel resistance produced the same rate of heating of the bottom and side of the shield and in no case did temperature differences develop that could affect the heat capacities by more than about 0.1%. It should be noted that the top and side of the shield were one piece.

The resistance thermometers were frequently compared against the laboratory standard thermocouples S-1.[3] It was found that in the course of the measurements the indications of thermocouple S-1 or of R-201 had changed by what corresponded to 0.085° at 20°K. and by 0.02° at 60°K. Past experience has shown that this change is probably in the thermocouple[5] and due to cooling; therefore, the thermocouple was calibrated against hydrogen vapor pressures by condensing liquid hydrogen in the can (14).[6]

It was then found that, at 20°K., the calibration of S-1 had changed 0.10°. The direction of the change was consistent with the changes in its comparison with R-201. On first cooling S-1 had thus differed from its original calibration by only 0.02°, which is within experimental error, and then slowly changed, R-201 remaining constant. Accordingly the original comparison of the resistance thermometer with S-1 was taken as giving most nearly the cor-

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[4] Johnston, *J. Opt. Soc. Am. and Rev. Sc. Inst.*, 17 (1928).

[5] Aston, "Temperature. Its Measurement and Control in Science and Industry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 219.

[6] This procedure was suggested by Professor K. S. Pitzer.

TABLE I

HEAT CAPACITY OF METHYLAMINE HYDROCHLORIDE

Molecular weight, 67.523; 0.68181 mole in calorimeter; 0°C. = 273.16°K.

Temp., °K.	C_p, cal./deg./mole	Series	Temp., °K.	C_p, cal./deg./mole	Series	Temp., °K.	C_p, cal./deg./mole	Series	Temp., °K.	C_p, cal./deg./mole	Series
	Beta form			Beta form (*contd.*)			Gamma form (*contd.*)			Gamma form (*contd.*)	
12.04	0.202	VII	156.39	16.428	I	96.68^a	13.256	IV	223.39	19.542	IV
13.10	0.251	VII	162.96	16.750	I	97.49	13.354	IV	227.93	19.882	IV
15.04	0.387	VII	169.66	17.106	I	102.21	13.740	VIII	229.41	19.774	IV
17.78	0.660	VII	176.66	17.456	I	104.66	13.916	III	235.89	19.997	IV
20.79	1.049	VII	183.41	17.776	I	107.60	14.145	VIII	237.70	20.35	V
23.98	1.536	VII	189.97	18.102	I	110.50	14.328	IV	242.25	20.26	IV
27.67	2.083	VII	196.49	18.360	I	111.41	14.356	III	246.55	20.39	V
31.28	2.794	VII	203.28	18.683	I	113.88	14.541	VIII	248.56	20.49	IV
35.11	3.409	VII	207.22	18.890	V	116.92	14.698	IV	252.79	20.58	IV
39.44	4.245	VII	210.09	19.045	I	123.96	15.144	IV	255.36	20.69	V
44.25	5.198	VII	213.33	19.233	I	130.24	15.491	IV	259.84	20.80	IV
49.14	6.058	VII	218.12	61.10	I	138.16	15.955	IV	264.15	461.2	IV
54.22	6.904	VII	220.31	114.44	I	146.44	16.384	IV	266.77	95.99	IV
57.53	7.435	VI	222.36	49.19	I	154.43	16.764	IV	272.07	22.58	IV
59.71	7.773	VII	220.04	Transition		161.79	17.091	IV	264.5	Transition	
62.20	8.169	VI		Gamma form		168.83	17.416	IV		Alpha form	
70.00	9.258	VI	19.55	1.426	IV	170.08^a	17.476	IV	227.20	20.48	II
76.32	10.145	VI	21.43	1.767	IV	170.39	17.577	III	233.05	20.40	II
82.36	10.874	VI	23.38	2.181	IV	175.67	17.778	IV	239.55	20.45	II
88.49	11.572	VI	26.13	2.652	IV	177.18	17.839	III	246.07	20.53	II
94.74	12.210	VI	30.31	3.450	IV	182.60	18.053	IV	253.06	20.60	II
99.09	12.600	I	34.75	4.403	IV	189.30	18.306	IV	259.06	20.73	II
101.08	12.800	VI	39.75	5.418	IV	195.90	18.564	IV	265.77	20.86	II
105.35	13.169	I	45.27	6.566	IV	196.13	18.587	III	265.97^a	20.87	IV
107.48	13.337	VI	51.23	7.562	IV	199.96	18.775	III	272.23	21.07	II
108.93	13.439	V	57.64	8.590	IV	202.42	18.796	IV	278.86	21.22	IV
111.74	13.621	I	63.09	9.435	IV	203.50	18.914	III	279.05	21.30	II
118.22	14.104	I	66.47	9.929	IV	206.46	19.054	III	279.29	21.30	V
120.68	14.246	V	71.71	10.635	IV	206.69	19.016	III	285.63	21.47	II
124.49	14.472	I	79.10	11.511	IV	208.86	19.057	IV	285.96	21.35	V
130.88	14.928	I	85.93	12.267	IV	212.70	19.172	IV	286.32	21.38	IV
135.06	15.174	I	90.16^a	12.677	IV	214.58	19.271	IV	289.79^a	21.55	IV
141.50	15.610	I	91.45	12.822	IV	216.44	19.325	IV	291.39	21.69	II
147.72	15.965	I	92.23	12.875	IV	218.75	19.382	IV	292.10^a	21.60	IV
153.84	16.261	I	96.26	13.243	VIII	222.46	19.601	IV	293.71	21.63	IV
									297.97	21.97	II

[a] Platinum-rhodium thermometer used as heater.

rect temperatures. As usual one defined calorie was taken equal to 4.1833 international joules.

The heat capacity measurements are tabulated in Table I and shown graphically in Fig. 2. The temperature rises can be estimated from the temperature interval between the mean temperatures of each point. The heat capacities are divided into three sections corresponding to the beta, gamma and alpha forms. The relation of the three different forms of methylammonium chloride is best shown by Fig. 3 in which the entropy is plotted against temperature. The room temperature form (alpha form) can be supercooled to about 220°K. when it changes irreversibly to the beta form. On heating the beta form to 220°K. a transition occurs extending over about 4° to the gamma form. The gamma form changes into the alpha form at 264°K. in a somewhat sharper transition. Providing it is not heated above this point the gamma form is easily supercooled and shows no tendency to go over into the more stable form. Thus starting with the gamma form between 220 and 264°K. it was easily possible to cool it down to 20°K. without any change to the stable beta form.

The time–temperature treatment of the methylamine hydrochloride with respect to the heat capacity measurements is as follows: The calorimeter was cooled rapidly to liquid air temperatures. Heat capacities were measured from 99.1 to 222.4°K. as Series I, which is part of the beta curve and beta transition. The calorimeter was then allowed to drift to room temperature. For Series II, the calorimeter was cooled slowly to 224.5°K. and heat capacities were taken to 300.6°K. No transitions were found, since the compound was in the alpha form. The calorimeter was then cooled to 202°K., left for twenty-four hours, then the heat of the lower transition was determined by heating to a point between the two transitions. Upon again cooling below the lower transition temperature, the heat capacities obtained were higher than Series I. Therefore, the compound had been supercooled, missing the lower transition; *i. e.*, it was in the gamma form. Since the material was apparently in a stable condition, the calorimeter was cooled to liquid hydrogen temperature, and the heat capacity measurements of Series IV were determined from 20°K. to room temperature. No transition was found at 220°, but one was found at 264.5°K.

On cooling the compound rapidly from room temperature to 117°K. in one hour the beta form was again obtained. The heat capacities of Series V were obtained while testing for equilibrium before and after check determinations of the heats of transition. The heat capacities of Series VI were taken on the beta form from 57°K. to overlap Series I. The compound was then cooled to solid hydrogen temperatures when Series VII was taken, overlapping Series VI. Series VIII on the high heat capacity curve (gamma form) was obtained after rapid cooling of the calorimeter, following a check determination of the heat absorbed in the 220.4° transition.

Above 80°K., the accuracy of the heat capacity measurements is about 0.1%. Below 40°K. the errors may approach 1%. From 28 to 40°K. this error is due to the rapid change in the derivative of the platinum–rhodium thermometer and its low sensitivity and the low sensitivity of the standard thermocouple in this region. The effect on the entropy is not this great as the major part of the error is not in the energy, *i. e.*, a few low heat capacities must necessarily be followed by some correspondingly high.

TABLE II

MOLAL HEAT CAPACITIES OF METHYLAMMONIUM CHLORIDE AT ROUNDED TEMPERATURES

Mol. wt., 67.523; 0°C. = 273.16°K.

Temp., °K.	Heat capacity, cal./deg./mole		Temp., °K.	Heat capacity, cal./deg./mole	
	Beta form	Gamma form		Beta form	Gamma form
12	0.200		160	16.60	17.01
15	0.380		170	17.12	17.47
20	0.936	1.503	180	17.62	17.93
25	1.696	2.426	190	18.10	18.33
30	2.517	3.395	200	18.63	18.71
35	3.390	4.452	210	19.05	19.08
40	4.369	5.479	220.4° transition		
50	6.196	7.371	220		19.44
60	7.829	8.977	230		19.80
70	9.309	10.40	240		20.14
80	10.60	11.62	250		20.48
90	11.73	12.67	260		20.80
100	12.71	13.57	264.5° transition		
110	13.56	14.31			Alpha form
120	14.22	14.90	270		21.07
130	14.91	15.50	280		21.32
140	15.49	16.05	290		21.55
150	16.06	16.56	295		21.66

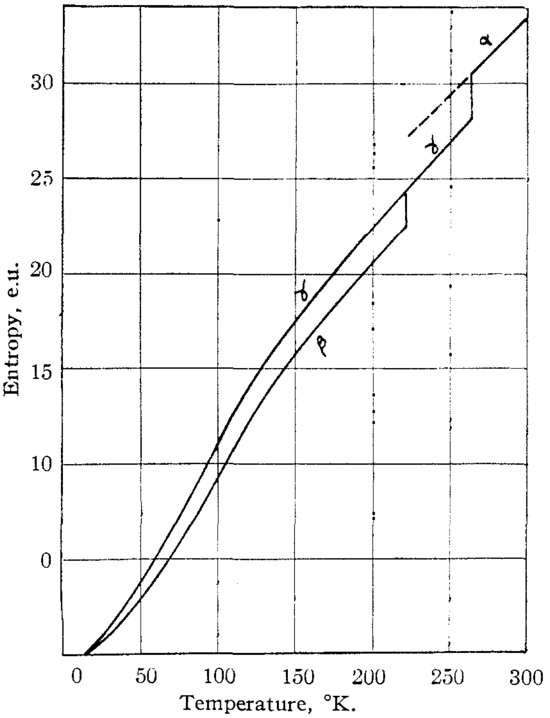

Fig. 3.—Temperature–entropy diagram for methylammonium chloride.

In Table II are listed values of the heat capacity at rounded temperatures. Above 40°K. these were obtained by plotting the deviations of the data from equations representing the data in the several ranges. Below 40°K. they were obtained graphically.

The Temperatures and Heats of Transition of Methylammonium Chloride.—The methods were as previously described,[7] with obvious modifications for the adiabatic method. The transition temperatures are tabulated in Table III while the

TABLE III

EQUILIBRIUM TEMPERATURES OF TRANSITION OF METHYLAMMONIUM CHLORIDE

Transformed, %	Total time, minutes	*T*, °K., Res. Th. R-201
	Lower Transition	
0		216.4
36.8	770	219.8
58.3	1530	220.8
80.0	2250	223.9
	Upper Transition	
0		263.8
49.8	1900	264.5
85.1	760[a]	266.0

[a] 85.1% converted in one heating period.

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(7) Aston and Messerly, THIS JOURNAL, **58**, 2354 (1936).

data for the lower and upper heats of transition are tabulated in Table IV.

TABLE IV

MOLAL HEAT OF TRANSITION OF METHYLAMMONIUM CHLORIDE

Mol. wt., 67.523; 0.68181 mole; 0°C. = 273.16°K.

Temperature interval, °K.	Corrected heat input, cal./mole	$\int C_p\,dT$, cal./mole	ΔH transition, cal./mole
Lower Transition at 220.4°K.			
211.948–233.236	1372.67	946.70	426.0
210.344–234.413	1494.12	1069.74	424.4
		Mean at 220.4°K.	425.2 ± 5
Upper Transition at 264.5°K.			
263.776–275.121	1210.70	532.63	678.1
262.274–276.886	1371.51	686.11	685.4
259.418–277.897	1531.92	866.75	665.2
259.742–282.345	1729.86	1064.02	665.8
		Mean at 264.5°K.	673.6 ± 10

Entropy of Methylammonium Chloride at 298.16°K. by Two Paths.—The entropy at 298.16°K. has been calculated by two paths: (a) that in which the beta form existed at 12.04°K. and was heated through the lower and upper transition and (b) that in which the gamma form existed at 19.0°K. and was heated through the upper transition only.

The calculation of the entropy is summarized in Table V. The graphical integrations were made by integrating under curves of the deviations from equations representing the heat capacity against log T and adding the result to that obtained by integrating the equations. As a check the heat capacities themselves were plotted against log T and the curves integrated by standard methods.

TABLE V

THE ENTROPY OF METHYLAMINE HYDROCHLORIDE

Mol. wt. 67.523

	e. u./mole
(a) Beta Form at 0°K.	
0–12.04°K., Debye extrapolation (θ = 200.5, 6 degrees of freedom)	0.067
12.04–220.4°K., graphical $\int C_p\, d \ln T$	22.326
220.4°K., (425.2/220.4) transition	1.929 ± 0.02
220.4–264.5°K., graphical $\int C_p\, d \ln T$	3.690
264.5°K., (673.6/264.5) transition	2.547 ± 0.04
264.5–298.16°K., graphical $\int C_p\, d \ln T$	2.555
	33.114 ± 0.07
(b) Gamma Form at 0°K.	
0–19.55°K., Debye extrapolation (θ = 173.1, 6 degrees of freedom)	0.442
19.55–264.5°K., graphical $\int C_p\, d \ln T$	27.610
264.5°K., (673.6/264.5) transition	2.547 ± 0.02
264.5–298.16°K., graphical $\int C_p\, d \ln T$	2.555
	33.154 ± 0.05

The excellent agreement between the entropy as calculated by the two paths either indicates that there is no randomness in either crystalline form or that both forms have the same degree of randomness.

Similar results have been obtained by Southard, Milner and Hendricks for normal amylammonium chloride.[8]

The Heat of Reaction of Aqueous Methylamine with Hydrochloric Acid.—The apparatus used for the measurements of the heat of neutralization and heats of solution was similar to that described by Giauque and Archibald,[9] except a standard quart Pyrex dewar was used (7 cm. i. d. and 30 cm. inside length) instead of a special dewar flask. The resistance thermometer of no. 40 B. and S. D. S. copper wire (resistance 46.8 ohms at 25°) encircled the stirrer shaft like that of Giauque and Archibald. However, it was wound on a copper tube with a soft soldered copper case gold plated on the outside. The current leads were no. 28 B. and S. D. S. copper while the potential leads were no. 32 B and S. D. S. copper. These were soldered to the no. 40 wire before it left the cylinder on which it was wound. The sample holder was mounted like that of Giauque and Archibald and broken with a plunger similar to theirs. However, this holder was a glass bulb of from 5 to 20 cc. capacity made from 1.0 cm. i. d. Pyrex tubing with a very thin bottom and top, the latter being concave to prevent the plunger sliding off. The bulb was held in a basket made of iron rod. This and the plunger as well as the stirrer were gold plated.

The addition of cooling coils below the surface of the solution and through which cold air could be blown proved extremely useful. Cold air was blown through these coils to bring the reaction mixture back to its initial temperature before taking the heat capacity of the system. The heat capacity was determined using the resistance thermometer as a heater, the lead corrections being about 0.16%. At least two (and usually three) heat capacity measurements were taken on each reaction mixture, after reaction, over the same temperature range as the heat of reaction measurements. This procedure was followed in all heat of reaction and of solution measurements. The heats obtained were therefore at the initial temperature.

In the determination of the heat of neutralization of aqueous methylamine, an approximately 0.10 weight normal aqueous solution of methylamine was prepared and titrated by weight against a hydrogen chloride solution which had been previously standardized against sodium carbonate using chlor phenol red as indicator. About 650 g. of solution was placed in the dewar while a known number of equivalents of approximately 5 weight normal aqueous hydrogen chloride in slight excess over the amine was placed in the glass bulb which was to be broken.

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[8] Southard, Milner and Hendricks, *J. Chem. Phys.*, **1**, 95 (1933).

[9] Giauque and Archibald, THIS JOURNAL, **59**, 561 (1937) (see Fig. 4 of their paper).

TABLE VI

HEAT OF NEUTRALIZATION OF LIQUID METHYLAMINE WITH 5.574 WT. MOLAL HYDROCHLORIC ACID AT 25°C.
HCl wt. molality based on Na_2CO_3: mol. wt. = 106.004

CH_3NH_2 soln. Wt. molality	CH_3NH_2 soln. Mass, g.	HCl soln. mass, g.	Heat evolved, cal.	Final wt. molalities (a) Salt	Final wt. molalities (b) Excess HCl	Corrected ΔH cal./mole Obs.	Corrected ΔH cal./mole Calcd.[a]
0.100636	628.57	13.1222	953.21	0.09898	0.01585	−13,248	−13,249
.100636	655.66	13.2814	990.36	.09902	.01240	−13,241	−13,249
.103375	625.97	12.3241	966.20	.10166	.00657	−13,257	−13,243
.108872	574.58	11.8055	931.16	.10711	.00592	−13,234	−13,231
.108872	587.25	11.7863	948.76	.10715	.00330	−13,225	−13,231
.112555	670.22	14.4116	1123.98	.11064	.00757	−13,222	−13,223
			Av.	.104		−13,238 ± 5	

[a] Calcd. from $\Delta H = -13{,}473 + 2260m$.

The results of the heat of neutralization experiments are summarized in Table VI. For the purpose of most simply dealing with the heat of dilution of the hydrogen chloride the results were corrected by subtracting the heat of dilution of the hydrogen chloride at its initial molality with the weight of water accompanying the amine. For this purpose the data of Rossini[10] were employed. The corrected molal heats in the last column were expressed as a linear function of the final molal concentration of salt by the method of least squares and from the resulting equation a value was obtained for the heat of neutralization at the average salt concentration (0.104 weight molal). From the method of correction it is obvious that, neglecting small dilution effects involving the excess of hydrogen chloride, to obtain the heat of neutralization of the gaseous amine by gaseous hydrogen chloride to form the solid salt, this result must be combined with the integral heats of solution of the gaseous hydrogen chloride, gaseous amine and the dry salt each to form a 0.104 molal solution in pure water. Of these it was necessary to determine the last two.

The Heat of Solution of Methylammonium Chloride in Water.—The results are summarized in Table VII. The methylammonium chloride purified as for the heat capacity measurements, was placed in the glass bulb to be broken and dried under a vacuum of 10^{-6} mm. of mercury and finally the bulb sealed off. Approximately 650 g. of water was placed in the dewar in each case.

TABLE VII

HEAT OF SOLUTION OF SOLID METHYLAMMONIUM CHLORIDE IN WATER AT 25°

Final cor. wt. molal	ΔH, cal./mole Obs.	ΔH, cal./mole Calcd.[a]
0.12398	1484	1485
.10668	1480	1475
.10019	1468	1471
.10353	1472	1473
.10400		1473 ± 3

[a] Calcd. from $\Delta H = 1410.5 + 602.7m$.

The heat of solution was obtained at a concentration of 0.104 molal by employing the same procedure as in the heat of neutralization measurements.

The Heat of Solution of Methylamine in Water.—The amine was condensed in the sample bulb after evacuation to 10^{-6} mm. of mercury. For this purpose the bulb was attached to the filling line with a ground glass joint. After filling it was sealed off from the line and weighed with the joint.

A gold-plated gauze cylinder fitted closely around the sample bulb. Its bottom and top were of gauze, the latter fitting tightly around the plunger. The purpose of this gauze cylinder was to break up bubbles of the amine when the sample bulb was broken by the plunger. The amount of amine dissolved as determined by titration was always a few tenths of a per cent. lower than that calculated from the weight. This circumstance was undoubtedly due largely to loss of amine after opening up the apparatus rather than during the experiments which were carried out in a closed system, so that the amount of amine dissolved was calculated from its weight.

The results are given in Table VIII, where the value at 0.104 molal was obtained as already described.

TABLE VIII

HEAT OF SOLUTION OF LIQUID METHYLAMINE IN WATER AT 25°

Final concn. wt. molal	ΔH, cal./mole Obs.	ΔH, cal./mole Calcd.[a]
0.10616	−5355	−5352
.10141	−5367	−5362
.10387	−5344	−5357
.10154	−5365	−5361
.12352	−5317	−5316
.10400		−5356 ± 6

[a] Calcd. from $\Delta H = -5570.1 + 2055m$.

From the value for the heat of solution of the liquid methylamine at 0.104 molal a value for the heat of solution of the gas at 1 atm. is obtained by combining with the calorimetric values for the heat of vaporization to the ideal gas at 1 atm. at 25°. This latter value is obtained from the real heat of vaporization at the normal boiling point by first correcting this to the ideal gas state. The correction is simply the difference in heat content between the ideal and real gas as given by the modified Berthelot equation

$$H - H^0 = \frac{9RP}{128}\left[\frac{T_c}{P_c} - 18\left(\frac{T_c^3}{P_c}\right)\frac{1}{T^2}\right]$$

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(10) Rossini, *Bur. Stds. J. Res.*, **9**, 679 (1932).

Taking $T_c = 430.1$°K. and $P_c = 73.6$[11]

$$\Delta H - \Delta H^0 = H - H^0 = -37.4 \text{ cal./mole}$$

Aston, Siller and Messerly[1] found the heat of vaporization to the real gas state at the normal boiling point to be 6169 ± 30 cal./mole. Thus the heat of vaporization to the ideal gas state is 6206 ± 30 cal./mole at the normal boiling point 266.84°K. The corresponding value at 298.16°K. is

$$\Delta H^0_{298.16} = 6206 + \int_{266.84}^{298.16} \Delta C_p^0 \, dT$$

where ΔC_p^0 is the difference between the heat capacities of the ideal gas, and the liquid, respectively. The latter can be obtained to 1% by extrapolation from the data of Aston, Siller and Messerly, the value obtained at 298.16°K. being 24.67 cal./deg./mole. To obtain the former we have compared the heat capacity data of Felsing and Jesson on the gas[12] (corrected to the ideal gas state using the modified Berthelot equation of state) with values calculated from the spectroscopic data of Owens and Barker,[13,14] using several assumed barriers hindering the internal rotation, by the tables of Pitzer.[15] By the method of least squares 2750 cal. was found to give the best fit and this value was then used to calculate the required values of the heat capacity. Table IX compares the calculated (using this barrier) and measured values of the molal heat capacity in the ideal state.

TABLE IX

HEAT CAPACITIES OF GASEOUS METHYLAMINE AT CERTAIN TEMPERATURES

Temp., °K.	C^0_p, cal./deg./mole Meas.[a]	Calcd.[b]
266.84 (b. p.)		11.57
273.16	11.45	11.73
298.16	12.71	12.36
323.16	13.63	13.02

[a] Felsing and Jesson, ref. 11. [b] From spectroscopic data with V = 2750 cal./mole for the potential hindering internal rotation.

The value thus obtained for ΔH of vaporization to the ideal gas state at 298.16°K. is 5811 ± 48 cal. The heat of solution of the ideal gas in water to yield a 0.104 molal solution is thus

$$\Delta H = -11{,}167 \pm 54 \text{ cal./mole}$$

The Heat of Reaction of Gaseous Methylamine with Hydrogen Chloride.—Combining the value for the heat of solution of gaseous methylamine with that of the heat of solution of gaseous hydrogen chloride at 1 atm. in water to yield a 0.104 molal solution, namely

$$\Delta H = -17{,}723 \pm 40 \text{ cal./mole}^{10}$$

and the value previously obtained for the heat of solution of methylammonium chloride in 0.104 molal solution, one obtains for the reaction

$$HCl(g) + CH_3NH_2(g) = CH_3NH_3Cl(s)$$
$$\Delta H^0 = -43{,}601 \pm 102 \text{ cal./mole}$$

This last value applies to the ideal gas state. The final heat of formation of the salt from the ideal gases may be too high by about 20 cal. due to neglect of the dilution effects, (a) the dilution of amine by the water in the hydrochloric acid, (b) the dilution of the excess hydrochloric acid to smaller concentrations than allowed for above, both of which are in the same direction. Thus the final value for the heat of neutralization may be in error by about 120 cal./mole assuming that all errors are additive.

The Free Energy of Dissociation of Methylammonium Chloride.—From the data presented in the last paragraph together with the entropies of the three substances ΔF^0 can be calculated for the reaction

$$CH_3NH_3Cl(s) \longrightarrow CH_3NH_2(g) + HCl(g) \text{ at } 298.16°\text{K.}$$

The entropy values at 298.16°K. are: HCl(g), 44.66 ± 0.00 e. u.,[16] CH_3NH_2(g), 57.73 ± 0.3 e. u.; CH_3NH_3Cl, 33.13 ± 0.05 e. u. From these, ΔS^0 for the reaction is 69.26 ± 0.35 e. u. and thus $\Delta F^0_{298.16}$ is 22,950 ± 144 cal./mole.

In computing the limits of error in the free energy it is to be noted that the error in ΔH due to the error of ±30 cal./mole in the heat of vaporization of the methylamine essentially cancels the error in $T\Delta S$ due to the same cause. It is to be noted if the orientation factor o is equal to 2 in $R \ln o$ for the entropy due to random orientation in the crystal the effect on the free energy as calculated from the heat of reaction and the third law of thermodynamics would be 298.16 $R \ln 2$ or 411 cal., so that it should be possible to detect 50% of the maximum randomness by comparison with accurate cell measurements.

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Summary

1. Methylammonium chloride has been shown to exist in three crystalline modifications designated alpha, beta and gamma.

2. The temperatures and heats of the transitions have been determined.

3. Heat capacity measurements have been made between 11°K. and room temperature on all three forms over the temperature range of their existence.

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(11) Berthoud, *J. chim. phys.*, **15**, 3 (1917).

(12) Felsing and Jesson, THIS JOURNAL, **55**, 4418 (1933).

(13) Owens and Barker, *J. Chem. Phys.*, **8**, 229 (1940).

(14) Aston and Doty, *ibid.*, **8**, 743 (1940).

(15) Pitzer, *ibid.*, **5**, 469 (1937).

(16) Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

4. Both the beta and the gamma forms can be cooled to below 20°K. the gamma being metastable. The same entropy (33.13 ± 0.05 e. u.) for the room temperature (alpha) form at 298.16°K. is obtained from heat capacities by two paths: (a) starting with the metastable gamma form below 20°K. and heating to the transition point to the alpha form (b) starting with the beta form, heating to and through the transition to the gamma form and then heating the gamma form to its transition to the alpha form. From these results it is considered unlikely that random orientation exists in either the beta or gamma forms at low temperatures.

5. Measurements have been made of the heat of reaction of aqueous methylamine with hydrochloric acid at 298.16°K. as well as of the heats of solution of liquid methylamine and solid methylammonium chloride in water. These results lead to a value of −43,601 ± 100 cal./mole for the heat of reaction of hydrogen chloride and gaseous methylamine.

6. The free energy of dissociation of methylammonium chloride at 298.16°K., calculated from the results, is $\Delta F^0 = 22{,}950 \pm 140$ cal.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary System Silver Sulfate–Sulfuric Acid–Water at 25°

BY EDWARD L. SIMONS[1] AND JOHN E. RICCI

Introduction.—The ternary system silver sulfate–sulfuric acid–water has not previously been reported in the literature, although the solubility of silver sulfate in aqueous solutions of sulfuric acid has been studied over limited ranges of acid concentration by Swann,[1a] Drucker,[2] and Akerlof and Thomas.[3] Kendall and Davidson,[4] however, investigated the binary system silver sulfate–sulfuric acid, and reported the existence of two addition compounds, $Ag_2SO_4 \cdot H_2SO_4$ and $Ag_2SO_4 \cdot 2H_2SO_4$, with the former, the bisulfate, existing in two polymorphic forms. The alpha modification, which crystallizes in thick prisms, is stable below 66°, while the beta modification, which crystallizes in fine needles, is stable above that temperature. By extrapolation, Kendall and Davidson determined the melting point of the bisulfate to be 125°. The transition point between the 1:2 salt and the alpha form of the bisulfate is at 36°. The metastable transition to the beta form occurs at 39°. Kendall and Davidson did not determine the solubility of the bisulfate in water, but the method of preparation of the normal sulfate from the bisulfate, described by Richards and Jones[5] and by Harkins,[6] indicates that the double salt is incongruently soluble. This is clearly shown in the ternary diagram constructed from data obtained in this investigation. Other addition compounds of the type $Ag_2SO_4 \cdot 3H_2SO_4 \cdot 2H_2O$ and $2Ag_2SO_4 \cdot 3H_2SO_4 \cdot 2H_2O$ are mentioned by Mellor[7] as having been reported in the older literature, but no evidence for such compounds has been found in the course of this investigation of the ternary system at 25°.

Materials.—Merck C. P. grade silver sulfate was used without further purification. The purity of the salt, as determined by titration of an aqueous solution of it with potassium thiocyanate, using the Volhard indicator, was 100.0 and 100.1%, respectively, for the two bottles used during the course of the investigation. Two stock solutions (72 and 98% by weight) of C. P. grade sulfuric acid were made up and analyzed by titration with sodium carbonate.

Solubility Determinations.—The solubility determinations were made according to the usual procedure described in similar investigations insofar as method of stirring, sampling, filtering, and temperature control are concerned. Through complexes of known composition, and analysis of the saturated solutions at equilibrium, the solid phases were determined by the usual methods of graphical or algebraic extrapolation, besides occasional analysis of centrifuged wet residues.

The analytical method involved determination of the silver sulfate concentration by titration with potassium thiocyanate using the Volhard indicator, and of the sulfuric acid concentration by titration with standard sodium hydroxide.

In the preparation of complexes care was taken to avoid the absorption of atmospheric moisture by solutions containing more than 70% by weight of sulfuric acid. Sampling of these complexes, high in sulfuric acid content, was done as rapidly as possible to minimize this effect, but nevertheless successive analyses of such solutions showed the composition to be changing slowly in a direction which would indicate that water was being absorbed from the atmosphere. For such concentrated solutions grease could not be used on the glass stoppers, and the use of paper filtering tips on the sampling pipets had to be dispensed with. These liquids were sampled after complete settling of the solid.

In the dilute solutions separate samples were taken for the acid and silver determinations, but for the more concentrated solutions both analyses were performed on the same sample. The acid analysis was made with

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(7) Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. III, Longmans Green, New York, N. Y., 1927, p. 452.