Dewar for the cooling bath. Stirring was continued, and the melting curve was determined. The freezing ranges were as indicated in the table.

The fact that $CH_2ClCClFCCl_3$ and $CHCl_2CClFCCl_3$ freeze almost at the same temperature is in good agreement with the close freezing points of $CH_2ClCCl_2CCl_3$ and $CHCl_2CCl_2CCl_3$.[2] These freeze at 30 and 29.5°, respectively.

Refraction.—The molecular refractions, MR_D, were calculated by means of the Lorentz–Lorenz formula. The atomic refraction for fluorine was obtained by subtracting from the molecular refraction the increments for carbon (2.418), hydrogen (1.100), and chlorine (5.967). This was done merely to obtain a confirmation of the gross formulas as the assumption cannot be made that the increments are absolutely constant.

Summary

$CH_3CClFCH_2Cl$ has been synthesized by addition of hydrogen fluoride to $CH_2{=}CClCH_2Cl$. The hydrofluorinated compound has been subjected to the action of chlorine in sunlight to yield $CH_3CClFCHCl_2$, $CH_3CClFCCl_3$, $CH_2ClCClFCCl_3$, $CHCl_2CClFCCl_3$ and $CCl_3CClFCCl_3$. As by-products, only a small amount of $CH_2ClCClFCHCl_2$ was isolated and traces of $CH_2ClCClFCH_2Cl$ were suspected. All the compounds have been tabulated and improved data for $CH_3CF_2CH_2Cl$ have been added.

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY

I. A Modified Heat Conduction Calorimeter[1,2]

BY WALDEMAR T. ZIEGLER AND CHARLES E. MESSER

The principle of the calibrated, heat-conduction calorimeter originally used by Andrews[3] has been the basis for a number of different calorimeters used by other investigators.[4] The simplicity and speed with which heat capacity data of adequate accuracy (1–3%) may be obtained, together with the fact that a continuous measurement of the change in heat content is simultaneously obtained, led the authors to choose this method as a means of determining the heat capacities of substances suspected of exhibiting anomalies of the type shown by ammonium chloride in the neighborhood of −30°. This paper presents a description of the construction, operation, and calibration of such a calorimeter, and an application of it to the study of the heat capacities of potassium chlorate, ammonium chloride and ammonium sulfate. These substances were chosen for study because their heat capacities had been determined by other investigators, and hence would permit an evaluation of the accuracy of the calorimeter. The experimental results for ammonium chloride would also permit the calculation of the entropy of this substance at 298.1°K. In later papers we shall present the results of similar studies of the thermal properties of cobaltous and cobaltic hexammine halides, and sodium and potassium cyanides.

The Heat Conduction Calorimeter

The determination of the heat capacity of a substance with a calibrated heat conduction calorimeter (see Fig. 1) is accomplished by comparing the time required to heat a known weight of the "unknown" substance through a definite interval of the temperature scale, with the time required to heat a known weight of a "standard" substance of known heat capcity through the same temperature interval under identical conditions (*i. e.*, the same temperature difference or "head" between mantle and calorimeter can, etc.) the time required to heat the empty can through the same interval having been determined previously. The mean molal heat capacity of the substance, C_{p_u}, in this interval may then be calculated from the expression

$$C_{p_u} = \frac{W_s M_u C_{p_s}}{W_u M_s} \times \frac{t_u - t_c}{t_s - t_c} \qquad (1)$$

In this expression t_u, t_s and t_c represent, respectively, the time (in seconds) required to heat W_u grams of the "unknown" substance (mol. wt., M_u), W_s grams of the "standard" substance (mol. wt., M_s), and the empty can through the *same* interval of the temperature scale. C_{p_s} is the mean molal heat capacity of the standard substance in this same temperature interval.

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(1) From a dissertation submitted to the Board of University Studies of The Johns Hopkins University by Waldemar T. Ziegler in conformity with the requirements for the degree of Doctor of Philosophy.

(2) Presented at the Symposium on Low-Temperature Research, Boston meeting of the American Chemical Society, September, 1939.

(3) Andrews, THIS JOURNAL, 48, 1287 (1926).

(4) Andrews and Haworth, *ibid.*, 50, 2998 (1928); Smith and Andrews, *ibid.*, 53, 3644 (1931); Stull, *ibid.*, 59, 2726 (1937).

The heat conduction calorimeters which have been described heretofore have been cooled by direct immersion of the mantle in the refrigerant. When the temperature of the calorimeter had been lowered sufficiently, the refrigerant was removed and heat capacity measurements were begun at once. This mode of operation possesses several undesirable features. In the first place, the sample is always cooled quite rapidly, particularly at the beginning. This sometimes results in the formation of unstable phases. This was strikingly shown in experiments on the octanols.[5] Of the fifteen structurally possible octanols studied by this method, nine were found to form glasses.

A similar difficulty might be expected to arise due to the rapid cooling of substances which exhibit lambda-type transitions, resulting in the "freezing in" of random orientations of the liberating groups or molecules involved. This state of non-equilibrium has been observed to occur in phosphine[6] and nickel hexammine nitrate[7] when these substances were cooled rapidly in a Nernst type calorimeter.

Another difficulty which is encountered in the operation of such "direct immersion" heat conduction calorimeters is that the temperature of the mantle continually increases, due to the continuous unchecked influx of heat from the environment. This results, in general, in no disadvantage, since the heating rate required to produce the desired temperature head is much greater than that arising from the heat leaks. However, during a phase transition the temperature of the sample becomes, of course, essentially constant, and the gradual influx of heat to the mantle may be large enough to prevent the maintenance of a constant temperature head between the calorimeter can and the mantle during the course of the transition, especially in the region 100–200°K. A similar difficulty may be expected to arise in the determination of the heat capacity of a substance exhibiting a lambda-type transition.

Apparatus.—We have attempted to remove the limitations mentioned above by setting the calorimeter assembly (C of Fig. 1) in a permanently fixed, liquid-nitrogen cryostat of the type described by Cardoso[8] and Keyes, Taylor and Smith.[9] Our cryostat consisted of two dewar vessels, A and B, one inside the other. The inter-wall space of dewar vessel B (the inner one) was connected to a high vacuum pumping system. With liquid nitrogen in dewar vessel A the calorimeter could be isolated from, or cooled slowly by, the refrigerant in A, depending upon whether or not the inter-wall space of dewar vessel B was evacuated or filled with a gas. Dry nitrogen gas was used as the exchange gas in the cavity of dewar vessel B (760 mm.), and the inter-wall space of B ($\sim$1.5 mm.).

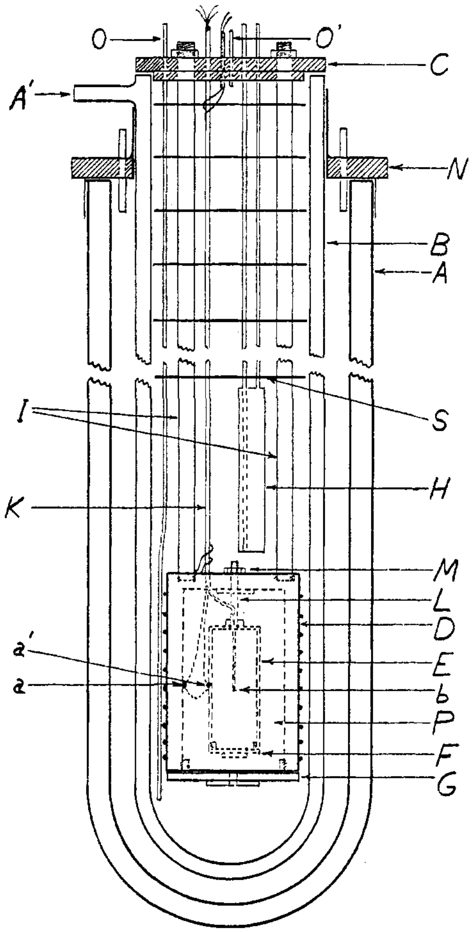

Fig. 1.—Diagrammatic sketch of calorimeter (not to scale).

The calorimetric assembly C consisted of the calorimeter mantle D, which completely surrounded the calorimeter can E, and the attendant supports and outlet tubes. The calorimeter mantle was a cylindrical copper shell, closed at the top by a cap and below by a perforated, threaded plug G. The mantle was 9.1 cm. long, had an outside diameter of 5.0 cm. and walls 4 mm. thick. On the outside of the mantle was wound a 30-ohm nichrome wire heater, imbedded in bakelite lacquer.

The cylindrical copper calorimeter can E was suspended from the top of the mantle by means of a bakelite rod L, fitted at the top with a nut M. The can was closed by

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[5] Cline and Andrews, This Journal, 53, 3668 (1931).

[6] Stephenson and Giauque, *J. Chem. Phys.*, 5, 149 (1937).

[7] Long and Toettcher, *ibid.*, 8, 504 (1940).

[8] Cardoso, *J. chim. phys.*, 13, 317 (1915).

[9] Keyes, Taylor and Smith, *J. Math. Phys. Mass. Inst. Tech.*, 1, 211 (1922).

means of a threaded plug F. The calorimeter can was 48 mm. long, had an outside diameter of 20 mm. and a wall thickness of 0.7 mm. A short section of german silver tubing, extending to the center of the can, served as a thermocouple well. The establishment of thermal equilibrium was hastened by inserting copper disks along with the sample whose heat capacity was to be measured.[10]

In order to minimize changes in the nature of the radiating surfaces of the can and mantle, these surfaces were oxidized to give a coating of black copper oxide as recommended by Stull.[4]

The calorimeter mantle was supported by two bakelite rods I and a german silver tube K which served as a conduit for the thermocouple wires. The various tubes which passed through the top of C formed vacuum-tight joints with the cover, which could be sealed to the top of dewar vessel B with a sealing compound. Tubes O and O′ were used to evacuate the space surrounding the calorimeter and to introduce the dry nitrogen gas which was used as the conducting gas. During a run O′ was closed and O was connected to a mercury bubbler and a 20-liter nitrogen storage bottle. This permitted the maintenance of a gas pressure in B which never varied by more than 2 cm. In order to facilitate cooling of the calorimeter a small. liquid nitrogen container H was placed just above the mantle. Immediately above H was located the first of six aluminum disks S which served both as radiation shields and to center the calorimetric assembly.

The temperature measuring system consisted of copper-constantan thermocouples, the junctions of the difference thermocouple being located at *a* and *a′*, the junction of the principal thermocouple being at *b*. The constantan wire was a portion of that used by Southard and Andrews[11] in the establishment of a temperature–e. m. f. table. Calibration of the couples was effected by direct comparison with a standard platinum resistance thermometer (LN No. 137184; NBS 499) in a cryostat using liquid pentane as a bath liquid, and by direct determination of the oxygen and sodium sulfate decahydrate points. The thermocouples were found to agree with the Southard–Andrews table to within 0.1° in the range −5000 to zero microvolts. Above 0° the observed e. m. f.'s were about 0.1° higher than this table. Above 35° the table constructed by Smith[12] was used as a basis for comparison. These tables, with the appropriate corrections, were then used in all temperature determinations, the ice-point being taken as 273.10°K. We estimate the accuracy of our temperature scale to be ±0.15° with respect to the International Temperature Scale. The agreement between our observed transition temperatures for ammonium chloride and sulfate and those obtained by other investigators is in accord with this estimate.[13]

Experimental Procedure.—With the calorimetric assembly in place liquid nitrogen was placed in dewar vessel A and the nitrogen container H. About two to three hours were required to cool the sample to 80°K. When the sample had been cooled to this temperature any liquid nitrogen remaining in H was removed, the heater on the mantle turned on, and a temperature head of 300 microvolts (approximately 15° at 100°K. and 7° at room temperature) established between the mantle and calorimeter can by regulating the current through the heater. The temperature head of 300 microvolts was maintained constant to ±1 microvolt throughout the run, which normally included the temperature range 100–320°K. Measurements of heat capacity were started as soon as the proper temperature head was established. Readings were made with two manually operated stop watches of the time required for the temperature of the sample to be increased by 200 microvolts, each succeeding interval beginning where the preceding interval ended. These microvolt intervals were always the same, and in all runs were taken between the same points on the temperature scale.

The duration of a run was about three hours for the empty calorimeter can, and five to seven hours for the loaded can. This corresponded to a heating rate of 0.4–0.6° per minute, depending upon the substance being studied. In the immediate neighborhood (*i. e.*, ±0.5°) of the heat capacity maxima for ammonium chloride and sulfate the heating rate fell to 0.1° per minute for a period of eight to ten minutes.

The maintenance of a constant temperature head of 300 microvolts presented no difficulties with any of the substances studied. Since approximately one-half of the total energy input to the mantle escaped to the liquid nitrogen cryostat, a decrease in the heating current produced an immediate decrease in the temperature of the mantle whenever such a change was required, as was the case, for instance, during the transitions in the ammonium salts studied. Furthermore, it was possible to maintain the sample at a constant temperature, if this was desired, or a portion of the temperature range under study could be reinvestigated by simply shutting off the heater and allowing the sample to cool again below the desired temperature range, after which the head could be reëstablished and measurements resumed.

It is also possible to determine the heat capacity of a substance as a function of *decreasing* temperature. Preliminary experiments indicated that a considerably smaller temperature "head" is required. The apparatus must be calibrated separately for these cooling experiments.

Two features of the operating procedure which had to be closely standardized were the loading operation and the adjustment of the level of the refrigerant in dewar vessel A at the beginning of a run. During the loading operation the calorimeter can was removed from the mantle, the thermocouple wires being sufficiently long to permit this. When the can was reinserted care was always taken to center the can, and to rearrange the wires in a close approximation to their former positions. Experiments showed that such removals resulted in only slight variations in the results obtained.

The necessity for an adjustment of the refrigerant level to a fixed point at the beginning of each run was borne out by experiment. It was found that the refrigerant level determined, to some extent, the temperature of the gas space above the mantle, especially when the refrigerant level was very low. This interdependence was reflected in

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(10) See Parks, THIS JOURNAL, **47**, 338 (1925).

(11) Southard and Andrews, *J. Franklin Inst.*, **207**, 323 (1929).

(12) R. H. Smith, Dissertation, The Johns Hopkins University, 1930, p. 37.

(13) See Table IV. The term "transition temperature" as used in this paper refers to the temperature at which the maximum heat capacity was observed in a given transition region.

the heating times obtained in different runs on the same sample for a given interval of the temperature scale, the time being smaller the higher the temperature of the gas space above the mantle. In all runs reported in this paper care was taken to adjust the refrigerant level to a fixed point at the beginning of each run.

Choice of a Standard Substance.—Potassium chloride was selected as the standard substance because it is an ionic substance similar to the others studied in this research, and because its heat capacity had been quite accurately determined employing an absolute method.[14] Since it was anticipated that measurements of heat capacity would be carried to 100°, some form of extrapolation of the experimental heat capacity of potassium chloride was necessary, there being no precise experimental results above 25°. The extrapolation procedure finally adopted made use of the expression

$$C_p = 6D(\theta/T) + (C_p - C_v) \qquad (2)$$

where $D(\theta/T)$ is the Debye heat capacity function. The Debye parameter, θ, was taken as 200,[15] the values of $C_p - C_v$ being calculated from the known coefficients of thermal expansion[16] and compressibility.[17]

The final selection of the standard heat capacity values for potassium chloride appear in Table II. The results are expressed in cal./mole/deg. (1 calorie = 4.1833 int. joules). The values up to 240°K. are the smooth curve values of Southard and Nelson, and are accurate to ±0.2%. Those above 240°K., which have been derived in the manner just described, are probably accurate, even at 100° to ±1%. Above 0° the expression $C_p = 12.10 + 3.97 \times 10^{-3}t$ (where t = °C.) represents the heat capacity values for potassium chloride to ±0.02 cal./mole/deg.

Materials: Potassium Chloride.—This material was Merck Reagent Grade. It was recrystallized once from water, dried for eighty hours at 110°, and finally heated for five hours at 700°. The material was then finely powdered.

Potassium Chlorate.—Baker C. P. material was recrystallized once from water and then dried for eighty hours at 110°.

Ammonium Chloride.—Baker C. P. material was used without further purification. It was powdered and dried in an oven for several hours at 90° to remove the last traces of moisture.

Ammonium Sulfate.—Baker C. P. material was recrystallized from a hot, saturated, water solution by adding 95% ethanol solution. The finely crystalline product was then dried for eighty hours at 110°.

Experimental Results

Using potassium chloride as a standard substance the heat capacities of potassium chlorate, ammonium chloride and ammonium sulfate have been determined in the range 100–320°K. The results reported are based on six runs made with the calorimeter can empty, and two standardization runs made using an 8.4333-g. sample of potassium chloride. Two runs were made using 10.61 g. of potassium chlorate, a single run using 8.526 g. of ammonium chloride, and three runs using a 6.376-g. sample of ammonium sulfate. All weights reported are on a vacuum basis.

Tables I, II and III contain a summary of the heat capacity measurements. The heat capacity values listed in Tables II and III refer to a temperature range which includes the heat capacity maximum. In this range temperature increments much smaller than 200 microvolts (~6°) were used, hence the accuracy of the derived C_p values is much less than at other temperatures. The temperature increments actually used are listed as ΔT, the maximum error in them being about ±0.02°.

TABLE I

MOLAL HEAT CAPACITIES

(0°C. = 273.10°K; 1 calorie = 4.1833 int. joules)

T, °K.	KCl	$KClO_3$	NH_4Cl	$(NH_4)_2SO_4$
107.2	9.65	15.8	9.4	20.5
117.1	10.02	16.0	9.9	22.1
126.2	10.33	16.8	10.8	23.9
135.0	10.58	17.4	11.5	25.8
143.3	10.78	17.6	11.9	27.1
151.4	10.93	18.4	12.4	28.9
159.2	11.06	18.1	12.9	30.4
166.7	11.18	18.7	13.5	33.0
173.9	11.28	19.3	14.3	35.6
181.0	11.36	19.5	15.0	38.0
187.8	11.44	19.7	15.8	40.3
194.5	11.51	19.9	16.0	42.9
201.1	11.58	20.0	16.2	46.1
207.4	11.63	20.1	17.0	50.2
213.7	11.70	20.3	17.9	55.1
219.8	11.76	20.6	18.6	
225.8	11.81	20.8	19.9	
231.7	11.86	21.3	22.0	41.5
237.5	11.90	21.4		42.5
243.2	11.94	21.8		43.4
248.8	11.98	21.7	18.7	43.6
254.4	12.01	22.2	18.5	44.2
259.8	12.03	22.5	18.6	44.4
265.2	12.05	22.9	19.1	45.0
270.4	12.07	22.9	19.1	45.0
275.6	12.11	23.4	19.1	45.8
280.8	12.13	23.5	19.6	46.1
285.9	12.15	24.0	19.6	46.1
291.0	12.17	23.8	19.8	46.5
296.0	12.19	24.0	20.0	47.1
301.0	12.21	24.1	20.2	47.4
305.9	12.24	24.2	20.3	47.7
310.7	12.26	24.2	20.2	48.1
315.5	12.28	24.2	20.2	48.4
320.2	12.30	24.1	20.0	48.5

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[14] Southard and Nelson, THIS JOURNAL, **55**, 4865 (1933); Nernst, *Ann. Physik*, **36**, 395 (1911); see also Magnus, *Physik. Z.*, **13**, 59 (1912).

[15] The choice of the value θ = 200 is based upon a consideration of the experimental data cited above,[14] and the assumption that C_v does not exceed the value 6 R at 100°.

[16] "International Critical Tables, Vol. III, p. 43.

[17] *Ibid.*, Vol. III, p. 50.

The heat capacities of the salts have been calculated from Equation (1), the heat capacities referring to the mean temperature of the 200 microvolt interval under consideration. The experimental values of t_c, t_s, and t_u for the various 200 microvolt intervals were always plotted against the mean temperatures corresponding to the intervals, and a smooth curve drawn through the experimental points. The values used in the calculation of the heat capacities were those read from the smooth curves.

Table IV contains a comparison of the experimentally determined transition temperatures and those obtained by other investigators.

TABLE II

MOLAL HEAT CAPACITY OF NH_4Cl IN THE TRANSITION RANGE

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
235.4	1.45	23.2	242.2	0.71	146
236.8	1.45	25.8	242.7	.29	50
238.2	1.45	27.1	243.0	.43	26
239.8	1.45	30.5	243.9	1.42	22.8
240.7	0.71	35	245.3	1.42	19.5
241.5	.71	43			

Time required to traverse range 235.4–245.3°K. = thirty-six minutes.

TABLE III

MOLAL HEAT CAPACITY OF $(NH_4)_2SO_4$ IN THE TRANSITION RANGE

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
218.3	1.50	62.5	223.2	0.30	1360
220.6	0.75	66	223.4	.75	380
221.7	.75	69	224.7	1.50	48.4
222.4	.30	78	227.3	3.00	42.1
223.0	.15	330			

Time required to traverse range 218.3–227.3°K. = twenty-five minutes.

TABLE IV

TRANSITION TEMPERATURES

NH_4Cl, °C.	$(NH_4)_2SO_4$, °C.	Observer
−30.5		Simon[18]
−30.4		Simon, v. Simson and Ruhemann[19]
−30.54 ± 0.10	−49.71 ± 0.20	Klug and Johnson[20]
	−50.7	Crenshaw and Ritter[21]
	−49.9	Nitta and Suenaga[22]
−30.5 ± 0.02° (warming)		Smits and MacGillavry[23]
−30.8 ± .02° (cooling)		
−30.6 ± .15	−49.9 ± 0.15	This research

Discussion of Experimental Results

Potassium Chlorate.—Our results for this substance are in good agreement with those obtained by Latimer, Schutz, and Hicks[24] employing an absolute method, the average percentage deviation of our results from theirs being 1.5%, our results being low.

Ammonium Chloride.—A comparison of our results for the heat capacity of this substance with those reported by Simon[18] throughout the range 107–290°K. showed, if the range 235–244°K. be excluded, an average percentage deviation of 1.2%, our results being low. Similar agreement with the results of Simon, v. Simson and Ruhemann[19] was obtained below 241°K. Above 244°K. our values of the heat capacity are 2.5–3% lower than the values reported by these investigators. In the portion of the transition range 235–242°K. there is considerable disagreement between our results and those of Simon,[18] our results being approximately 5% higher and more nearly in accord with those reported by Simon, v. Simson and Ruhemann. In the region of maximum heat capacity (242–244°K.) all three researches differ widely. This disagreement may be due to varying degrees of non-equilibrium variations in the choice and accuracy of measurement of temperature intervals, as well as differences of the order of a tenth of a degree in the different temperature scales.

The "heat of transition," ΔH_{Tr}, of ammonium chloride was determined in the following rather arbitrary manner. The experimental values of C_p were plotted as a function of the temperature, and a smooth curve drawn connecting the points below the transition range with those above it. The curve so obtained included the temperature range 201.1–254.3°K., and was considered to represent the "normal" heat capacity of ammonium chloride in the transition range. The equation C_p (normal) $= 6.97 + 4.49 \times 10^{-2}\ T(T = °\mathrm{K.})$ represents our choice of the "normal" heat capacity within 0.5%. We then calculated the "normal" change in heat content, ΔH_{N}, in the temperature range 201.1–254.3°K. Since the experimental method used measured the total change in heat content, ΔH (= 1184 cal. per mole), in this interval, we obtained, by difference, $\Delta H_{\mathrm{Tr}} = \Delta H - \Delta H_{\mathrm{N}} = 267$ cal. per mole. This may be compared with the value 356 cal. per mole calculated in a similar manner by Simon[18] using the data of Ewald.[25] The higher value obtained by Simon is very probably due to

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[18] Simon, *Ann. Physik*, **68**, 241 (1922).

[19] Simon, v. Simson and Ruhemann, *Z. physik. Chem.*, **129**, 339 (1927).

[20] Klug and Johnson, THIS JOURNAL, **59**, 2061 (1937).

[21] Crenshaw and Ritter, *Z. physik. Chem.*, **16B**, 143 (1932).

[22] Nitta and Suenaga, *Bull. Chem. Soc. Japan*, **13**, 36 (1938).

[23] Smits and MacGillavry. *Z. physik. Chem.*, **A166**, 97 (1933).

[24] Latimer, Schutz and Hicks, THIS JOURNAL, **56**, 88 (1934).

[25] Ewald, *Ann. Physik*, **44**, 1213 (1914).

the wider temperature range (approximately 140–260°K.) used.

In order to test the agreement between our calorimetric results and those of Ewald we have used his value of the mean heat capacity of ammonium chloride in the range −77 to 0°, namely, 21.42 cal., to calculate the total change in heat content of the salt in this range. The result obtained is 1649 ± 3 cal. For the same temperature range we found the value 1619 ± 10 cal./deg./mole, a difference of 1.8%. When our choice for the "normal" C_p is combined with the data of Ewald mentioned above one obtains for ΔH_{Tr} the value 297 cal. per mole.

The Entropy of Ammonium Chloride.—Since the experimental method used measured the total energy input as the region of maximum heat capacity was traversed, it is possible to make a reasonably reliable calculation of the entropy change in this region. We have been able, therefore, to calculate the entropy of ammonium chloride at 298.1°K., employing the data of Simon[18] below 100°K. Table V summarizes the calculation.

TABLE V

Range, °K.	Entropy change, e. u.
0–20	0.11 ($\theta_D = 280$)
20–100	5.76
100–231.7	11.10
231.7–251.6	2.35
251.6–298.1	3.26
	$S_{298.1} = 22.6 \pm 0.3$

Kelley[26] using the data of Simon[18] and Simon, v. Simson and Ruhemann,[19] has made an approximate calculation of the entropy of ammonium chloride, obtaining the value 31.8 e. u., of which one-third arises in the immediate neighborhood of the heat capacity maximum. Kelley himself pointed out that the error involved in his calculation of this contribution might be quite large. We have found a contribution to the entropy of 2.35 e. u. for the temperature range 231.7–251.6°K., which includes the heat capacity maximum.[27]

Ammonium Sulfate.—Heat capacity measurements have been carried out over an extended range of temperatures by Ewald,[25] Crenshaw and Ritter,[21] and Nitta and Suenaga.[22] The results reported by these investigators differ widely, the results of Crenshaw and Ritter being as much as 10–30% higher than those found by Ewald, and Nitta and Suenaga throughout the temperature range where comparison is possible (190–290°K).

A comparison of our results with those discussed above shows, on the whole, fairly good agreement with those reported by Ewald, and Nitta and Suenaga. In the range 107–170°K. our results lie about 6% below those of Nitta and Suenaga. Above 170°K. the two sets of results agree quite well, with the exception of the region in the immediate neighborhood of the transition, namely, 218–225°K., the average percentage deviation being 1.6%. In the range 218–225°K. our measurements are 5–10% lower than those of Nitta and Suenaga for those values for which a comparison can reasonably be made.

Unfortunately, these results reported by us cannot be considered as settling the problem of the true heat capacity of ammonium sulfate.[28] Rather they permit a decision to be made between the widely divergent results of Crenshaw and Ritter and those of Nitta and Suenaga, those of the latter being certainly more nearly correct.

Acknowledgment.—The authors thank Dr. D. H. Andrews and Dr. E. R. Blanchard for many valuable suggestions relative to the design and operation of the calorimeter herein described. One of us (W. T. Z.) expresses his appreciation for the financial assistance given him by the Rotary Educational Foundation of Atlanta, Incorporated, while a student at The Johns Hopkins University.

Summary

1. A modified heat conduction calorimeter suitable for the study of the thermal properties of

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[26] Kelley, U. S. Dept. of Commerce, Bur. of Mines Bull. No. 350, p. 37 (1932).

[27] This entropy change was computed from the expression $\Delta S = \sum_i \frac{\Delta H_i}{T_{mi}}$, where ΔH_i represents the experimentally observed change in the heat content of the sample (calculated on a molal basis) in the ith temperature increment of the above range, and T_{mi} represents the mean temperature of this ith interval in °K. Altogether, eight intervals were included. This method of calculation of the entropy change gives results which are certainly accurate to better than 0.05 e. u.

[28] A recent redetermination of the heat capacity of ammonium sulfate in this Laboratory, using a new calorimeter of similar design and some of the same ammonium sulfate sample, has given values of C_p in substantial agreement with those reported in this research in the region 107–170°K. In the region 170–230°K. (excluding the interval in the immediate neighborhood of the heat capacity maximum) the newer values are consistently 3–5% below those reported in this paper, and above 230°K. are uniformally 6–8% lower, being at 302°K. in good agreement with a value (44.80 cal./deg./mole) found by Ewald.[25] Since redeterminations of the heat capacities of ammonium chloride and potassium chlorate using the new calorimeter gave results in good agreement with results reported in this paper, we feel that the discrepancy is associated with the ammonium sulfate itself, non-equilibrium conditions arising from the transition being the probable source of the difficulty.

substances exhibiting transitions of the lambda-type has been described.

2. The heat capacities of potassium chlorate, ammonium chloride and ammonium sulfate have been redetermined in the temperature range 107–320°K., using potassium chloride as a standard substance.

3. The entropy of ammonium chloride at 298.1°K. has been calculated.

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

II. The Heat Capacities of Some Cobalt Hexammine Halides

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Some years ago Kracek, Hendricks and Posnjak[3] pointed out that the interpretation of the crystal structure data found by Wyckoff[4] for nickel hexammine nitrate was probably incorrect and suggested that a more nearly correct interpretation involved a rotational motion of the nitrate ions, thus giving a structure similar to that of calcium fluoride, with the $Ni(NH_3)_6^{++}$ ions corresponding to the calcium ions and the nitrate ions to the fluoride ions. Recently Yu[5] has redetermined the structure of nickel hexammine nitrate, and has concluded that the nitrate ions oscillate with abnormally large amplitudes about their nitrogen atoms as centers, the configuration of equivalent nitrate ions in different unit cells being not always the same. The $Ni(NH_3)_6^{++}$ ions showed no such motion.

The thermal properties of this substance also have been investigated. Jensen and Beevers,[6] employing the method of differential cooling curves, discovered a lambda-type transition at −28.6°. More recently the heat capacity of this substance has been determined in the range 54–300°K. by Long and Toettcher.[7] These investigators found a lambda-type transition at −30°, and a region below 85°K. in which the heat capacity was slightly anomalous. Due to the large entropy of transition observed, 7.65 ± 0.5 e. u., Long and Toettcher concluded that both the ammonia molecules and the nitrate ions are involved in the transition, and that the transition could best be described as a random arrangement of these groups about their characteristic equilibrium positions. From the fact that nickel hexammine chloride exhibits no thermal anomaly in the range −180 to 20°,[6] these investigators concluded that "the presence of the nitrate groups would seem to be required for the occurrence of the transition."

About two years ago the author measured the heat capacities of $Co(NH_3)_6I_2$, $Co(NH_3)_6Cl_3$ and $Co(NH_3)_6I_3$ in order to determine whether or not transitions of the lambda type might be associated with the thermal motions of the ammonia molecules in these complexes. This paper contains the results of that study, and indicates that a lambda-type transition occurs in $Co(NH_3)_6I_3$, which must be associated with the motions of the ammonia molecules.

Experimental Part

Preparation of Materials. Cobaltous Hexammine Iodide.—This salt was prepared according to the "wet" method of Biltz and Fetkenheuer.[8] It was dried in a desiccator over solid potassium hydroxide. The resulting salt was pink in color—% NH_3: calcd., 24.63; found, 24.63, 24.65; estimated purity, 99.8%.

Cobaltic Hexammine Chloride.—This salt was prepared according to the method of Biltz.[9] The salt was recrystallized once from hot dilute hydrochloric acid solution, washed with cold water, dried in air and finally heated in an atmosphere of ammonia for six hours at 90° and one hour at 100°. The crystalline product was reddish-orange in color—% NH_3: calcd., 38.20; found, 38.24, 38.06; estimated purity, 99.8%.

Cobaltic Hexammine Iodide.—This salt was prepared according to the method of Fremy,[10] except that the cobaltic hexammine chloride was used as the starting material instead of the nitrate. The resulting product was recrystallized first from water, then from dilute hydriodic acid solution and finally from water by rapid cooling. It was dried for ten hours at 45° and then in an atmosphere of ammonia for two hours at 105°, after which time its weight

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[1] From a dissertation submitted to the Board of University Studies of The Johns Hopkins University by Waldemar T. Ziegler in conformity with the requirements for the degree of Doctor of Philosophy.

[2] From a paper presented at the Symposium on Low-Temperature Research, Boston meeting of the American Chemical Society, September, 1939.

[3] Kracek, Hendricks and Posnjak, *Nature*, **128**, 410 (1931).

[4] Wyckoff, THIS JOURNAL, **44**, 1260 (1920).

[5] Yu, *Nature*, **141**, 158 (1938).

[6] Jensen and Beevers, *Trans. Faraday Soc.*, **34**, 1478 (1938).

[7] Long and Toettcher, *J. Chem. Phys.*, **8**, 504 (1940).

[8] Biltz and Fetkenheuer, *Z. anorg. Chem.*, **89**, 130 (1914).

[9] Biltz, *ibid.*, **83**, 177 (1913).

[10] Fremy, *Ann.*, **83**, 289 (1852).