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.

BALTIMORE, MD. RECEIVED APRIL 4, 1941

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

II. The Heat Capacities of Some Cobalt Hexammine Halides

BY WALDEMAR T. ZIEGLER[1,2]

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).

became constant. The crystals from water were deep red in color; in a fine state of subdivision they were reddish-orange—% NH_3: calcd., 18.86; found, 18.87, 18.78; estimated purity, 99.6%.

Calorimetric Measurements.—The calorimetric measurements were made with a modified heat conduction calorimeter, the construction and calibration of which has been described previously.[11] Potassium chloride was chosen as the reference substance. The experimental technique employed and the treatment of the experimental data obtained also have been discussed in detail in I and will not be repeated here.

Two runs were made on each substance, 6.713 g. (0.01617 mole) of $Co(NH_3)_6I_2$, 9.903 g. (0.03703 mole) of $Co(NH_3)_6Cl_3$, and 10.725 g. (0.01979 mole) of $Co(NH_3)_6I_3$ being used. All weights reported are on a vacuum basis.[12] The data obtained for each pair of runs have been averaged and the heat capacities calculated from these average values. The

TABLE I

THE MOLAL HEAT CAPACITIES OF COBALTOUS HEXAMMINE IODIDE AND COBALTIC HEXAMMINE CHLORIDE AND IODIDE

0°C. = 273.10°K. 1 cal. = 4.1833 int. joules

T, °K.	$Co(NH_3)_6I_2$	$Co(NH_3)_6Cl_3$	$Co(NH_3)_6I_3$
107.2	48.9	43.5	45.4
117.1	48.6	45.6	47.0
126.2	50.8	48.5	50.2
135.0	53.2	51.2	52.1
143.3	54.6	52.5	53.1
151.4	56.7	54.2	55.2
159.2	57.4	55.3	56.4
166.7	58.5	57.1	57.8
173.9	59.5	58.7	59.9
181.0	60.5	60.7	60.8
187.8	61.0	62.1	61.6
194.5	61.6	62.5	62.0
201.1	61.7	63.0	62.4
207.4	62.1	63.7	64.8
213.7	62.8	64.5	64.4
219.8	63.6	65.1	65.0
225.8	63.8	66.0	65.7
231.7	64.3	67.3	66.7
237.5	64.9	68.0	67.9
243.2	65.2	69.4	68.8
248.8	65.5	69.9	69.1
254.4	66.3	71.2	70.6
259.8	66.2	71.5	70.7
265.2	67.1	72.4	72.1
270.4	66.0	72.6	72.7
273.8			95.4
275.6	66.9	73.8	
277.0			140
280.8	67.3	74.7	96.6
285.9	68.2	74.5	85.0
291.0	68.3	75.5	73.5
296.0	69.1	76.1	73.8
301.0	69.4	77.4	75.0
305.9	69.9	76.8	73.7
310.7	71.1	76.7	74.5
315.5	71.5	76.8	75.3
320.2	72.1	77.2	76.0

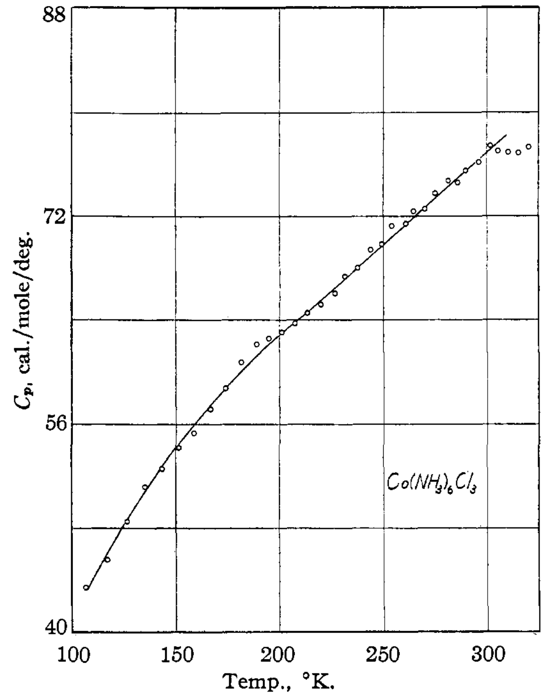

Fig. 1.—Heat capacity of $Co(NH_3)_6Cl_3$ in calories per mole per degree.

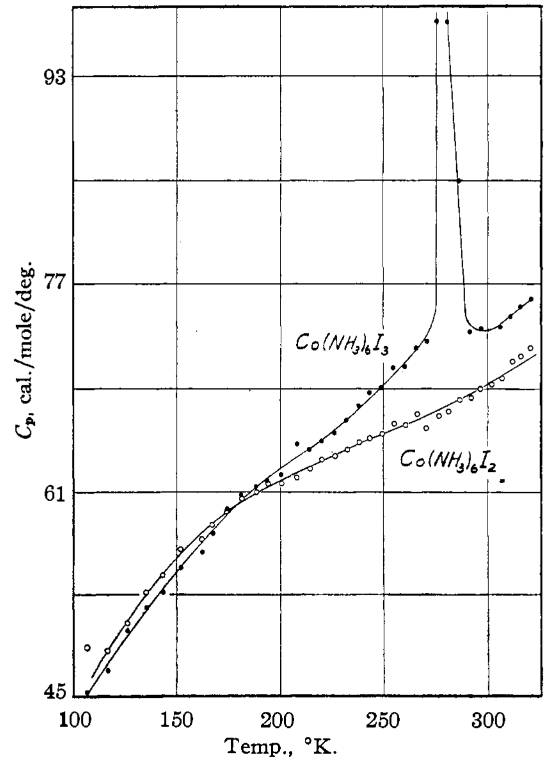

Fig. 2.—Heat capacity of $Co(NH_3)_6I_2$ and $Co(NH_3)_6I_3$ in calories per mole per degree.

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[11] Ziegler and Messer, THIS JOURNAL, **63**, 2694 (1941), hereafter referred to as I.

[12] The densities given by Biltz and Birk, *Z. anorg. Chem.*, **127**, 34 (1923), were used.

results of the measurements are given in Table I and are presented graphically in Figs. 1 and 2. These results are estimated to be correct to 1.5–2%, relative to the values chosen for KCl.[11]

Discussion of Results

On the whole the heat capacities of the three salts do not differ markedly from each other for a given temperature. The heat capacity of the cobaltic hexammine iodide was found to be somewhat greater than that of the chloride and slightly less than that of the cobaltous salt at low temperatures, while at higher temperatures (180–270°K.) the heat capacities of the former two salts coincided. In the region 270–290°K. the cobaltic hexammine iodide exhibited a region of anomalous heat capacity having a maximum at 277.4 ± 0.5°K. Above 290°K. the heat capacity of the cobaltic hexammine iodide was found to be approximately two calories below that of the chloride, and four calories above that of the cobaltous iodide. No previous heat capacity measurements appear to have been made on these substances.

The characteristics of the region of anomalous heat capacity are those usually associated with a lambda-type transition of the sort observed in ammonium chloride at −30°. Calculation of the "heat of transition"[13] yielded a value of 420 cal. per mole. This value may be in error by as much as 5%, due to the small heat effect actually observed. The transition is accompanied by no obvious change in color.[14]

The question of the probable origin of this anomalous heat capacity or transition in the cobaltic hexammine iodide immediately presents itself. Several obvious possibilities which must be considered are: (1) an electronic transition of the Schottky type; (2) a first order phase transition; (3) a "rotational" transition in the sense that the term has been used by Pauling[15]; (4) an order–disorder phenomenon of the type which seems to occur in ammonium chloride.[16] Of these possibilities the first seems to be excluded, since the observed transition takes place within such a small temperature interval.

TABLE II

Substance	Crystal system	Lattice constant, Å.	Co-N distance, Å.
$Co(NH_3)_6Cl_3$	Monoclinic[17]		Unknown[20]
$Co(NH_3)_6Br_3$	Rhombohedral[18]		Unknown[20]
$Co(NH_3)_6I_3$	Cubic[19]	10.9	1.9
$Co(NH_3)_6I_2$	Cubic[19]	10.92	2.7

The crystal structure data available for the substances studied are summarized in Table II, the data for the bromide being included for comparison. The data refer to room temperature. The possibility that the observed thermal effect (on cooling) was due to a first-order phase transition from the cubic to, perhaps, the rhombohedral system was considered. Studies made of the crystals with a polarizing microscope[21] at room temperature and in the neighborhood of −50° indicated that the crystals were isometric both above and below the transition. Furthermore, crystals of the material showed no tendency to cloud or fracture when immersed in liquid nitrogen. Hence, if a phase transition occurs it must be from one cubic structure to another.[22] However, the diffuseness of the transition militates against the occurrence of such a first-order transition.

The origin of a "rotational" motion in the cobaltic hexammine iodide is limited to two possibilities: (1) the rotation of the $Co(NH_3)_6^{+++}$ ion as a unit, and (2) the rotation of the ammonia molecules about their cobalt–nitrogen bonds. The first possibility may be eliminated on the basis of the known structure of the solid at room temperature. Hence, we are forced to conclude that the transition is associated with the motion or orientation of the ammonia molecules about their Co–N bonds. The transition may be due to the onset of a more or less restricted rotation of the ammonia molecules about the Co–N bonds, or to change from an ordered arrangement of the hydrogen atoms of the ammonia molecules in the several equilibrium positions associated with their environment in the crystalline solid (result-

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(13) For method of calculation see I.

(14) The observed heat effect corresponds to a 1.1% water content. The possibility that the anomaly was due to occluded water seems to be eliminated on the following grounds. The sample had been dried to constant weight (±0.1%), and was not hygroscopic. Furthermore, the anomaly extended over the region 270–290°K., and the heat capacity above this region was 1.5–2 cal. per mole *less* than that of the chloride, although in the range 200–270°K. the heat capacities of these two substances were almost identical. If the anomaly had been due to water one might expect the region of the anomaly to be considerably smaller, and the heat capacity above this region to be approximately equal to or somewhat greater than that of the chloride.

(15) Pauling, *Phys. Rev.*, **36**, 430 (1930).

(16) (a) Menzies and Mills, *Proc. Roy. Soc.* (London), **148**, 407 (1935); (b) Eucken, *Z. Elektrochem.*, **45**, 126 (1939).

(17) Groth, "Chemische Krystallographie," Vol. I, 1906, p. 264.

(18) Jörgensen, *J. prakt. Chem.*, **35**, 430 (1887).

(19) Ewald and Hermann, "Strukturbericht" (1913–1928); *Z. Krist.*, Ergänzungsband, 431, 437, 458 (1931).

(20) The crystal structure of these compounds has not been investigated.

(21) The author is indebted to Dr. W. J. Kirkpatrick for help in carrying out these studies.

(22) X-Ray studies of the transition are now in progress to settle this point.

ing in strict periodicity of structure) to a random distribution of the hydrogen atoms among these equilibrium positions (resulting in aperiodicity of structure as far as the positions of the hydrogen atoms in the crystal as a whole are concerned). It is not possible to decide between these two alternatives with the experimental data available at the present time.[23]

Summary

The heat capacities of cobaltous and cobaltic hexammine iodide and cobaltic hexammine chloride have been measured with an accuracy of 1.5–2% throughout the range 107–320°K. by means of a calibrated heat conduction calorimeter, using potassium chloride as a standard substance. The cobaltic hexammine iodide has been found to exhibit an anomalous heat capacity in the region 270–290°K., with a maximum at 277.4 ± 0.5°K. Evidence is adduced which indicates that the origin of the thermal effect is to be associated with the thermal motion of the ammonia molecules about their Co–N bonds.

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[23] A consideration of the spatial arrangements of the ammonia molecules in crystalline cobaltous and cobaltic hexammine iodides indicates that in neither crystal at room temperature is there sufficient room for a free rotation of the ammonia molecules about their Co–N bonds. This fact makes the difference in behavior of these two salts somewhat less strange. (No transition was found in $Ni(NH_3)_6Cl_2$, where similar spatial arrangements and conclusions apply.[6]) It is possible that the transition would occur in the cobaltous hexammine iodide in a temperature region other than that investigated in this research. It is planned to study both substances at higher and lower temperatures in the near future.

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

III. Rotation of Groups in Ionic Lattices. The Heat Capacities of Sodium and Potassium Cyanides[1,2]

BY CHARLES E. MESSER AND WALDEMAR T. ZIEGLER

Introduction

Heat capacity measurements have proved of great value in the study of the so-called "rotational transitions" of the type shown by ammonium chloride at −30°.[3] While the chief value of such measurements lies in their detection of the energy absorption in these transitions, it is also possible to analyze the numerical values of the heat capacity of a substance outside of a transition region and to draw conclusions as to the rotational freedom of motion of its component ions or molecules from such an analysis. Eucken[3] has done this for many molecular and ionic substances.

The available literature dealing with the alkali metal cyanides strongly indicates their possession of transitions of this type. The alkali cyanides at room temperature have the same cubic structure as the corresponding chlorides or bromides.[4] On this basis Wyckoff[5] has stated that the cyanide ions are probably rotating in these salts. The calculations of Sherman[6] on the crystal energies of the alkali cyanides further support this assumption. Finally, Bijvoet and Verweel[7] have confirmed the existence of a transition in sodium cyanide between 11 and 16° by visual observation and by crystal structure methods. The structure above the transition is the face-centered cubic structure of the sodium chloride type, while that reported below the transition is orthorhombic, with all of the cyanide ions aligned in the direction of the *b*-axis of the unit cell.

Sodium and potassium cyanides were chosen as objects of research because of this evidence of rotational transitions and because their relatively simple structures might make the results capable of theoretical interpretation. No previous heat capacity measurements on these substances appear to have been made.

Experimental

The heat capacity measurements were made by means of a calibrated heat conduction calorimeter similar in principle and design to the one previously described.[8] Since the apparatus, ex-

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

[2] Acknowledgment is made of a grant-in-aid from the Hynson, Westcott and Dunning Research Fund.

[3] Eucken, *Z. Elektrochem.*, **46**, 126 (1939), and Smyth, *Chem. Rev.*, **19**, 329 (1936), give comprehensive reviews of the experimental and theoretical background of this field.

[4] Natta and Passerini, *Gazz. chim. ital.*, **61**, 191 (1931).

[5] Wyckoff, "The Structure of Crystals," Chemical Catalog Company, New York, N. Y., 1931.

[6] Sherman, *Chem. Rev.*, **11**, 149 (1932).

[7] (a) Bijvoet and Verweel, *Rec. Trav. Chim.*, **54**, 631 (1935); (b) Verweel and Bijovet, *Z. Krist.*, **100**, 201 (1938).

[8] Ziegler and Messer, THIS JOURNAL, **63**, 2694 (1941), hereafter referred to as Paper I.