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]

[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.

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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[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.*, **45**, 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.

perimental procedure and calculations in the present research were essentially the same as those described in Paper I, it is sufficient to describe here only the significant changes made in the present research.

Apparatus.—A gold calorimeter can of the same size was substituted for the copper can of the earlier research because of the very slow rate of corrosion of gold by cyanides, as compared with the rate for copper.[9] Provisions were made to fill and empty the can without removing it from the mantle, thus eliminating any errors which might have arisen from its removal and reinsertion.

The chief innovation in the present research was the use of different media in the outer thermostat for measurements in different temperature regions, instead of the previous, single, fixed, liquid-nitrogen cryostat.[8] It was desired to extend the measurements up to 100°, and the necessary maintenance of a high liquid nitrogen level would have been difficult with such high temperatures inside the apparatus. The following media were employed in the outer thermostat for heat capacity measurements over the temperature ranges given: (1) liquid nitrogen at 77°K. for measurements over the range 90 to 240°K.; (2) a carbon dioxide–acetone mixture at 195°K. for the range 200 to 300°K.; (3) an ice–water mixture at 273°K. for the range 273 to 373°K. The upper limits of the first two ranges were so chosen as to overlap the lower portion of the next higher range, enabling the heat capacity values in these overlap ranges of temperature to be checked by two sets of measurements, each with the outer thermostat at a different temperature.

Materials.—The samples of potassium chloride, potassium chlorate and ammonium chloride used in the calibration and testing of the apparatus were portions of the preparations previously used (*cf.* Paper I) and were redried for several hours at 100°.

The samples of sodium and potassium cyanides were prepared by the addition of liquid hydrogen cyanide to absolute alcoholic solutions of sodium ethoxide and potassium hydroxide, respectively. The sodium cyanide was recrystallized twice from absolute methanol solution by evaporation with a stream of nitrogen gas.[10] The two salts were dried in a vacuum at 120–130°. They were analyzed by the Liebig titration method with silver nitrate. The results of the analysis indicated in each case a purity of 99.7% or better. *Anal.* Calcd. for NaCN: CN, 53.08. Found: 52.93. Calcd. for KCN: CN, 39.96. Found: 39.85, 39.90.

Procedure and Calculations.—The experimental procedure was the same as that described in Paper I except as influenced by the use of different media in the outer thermostat. In the usual procedure for a substance the runs with the thermostat at 77°K. were made first, then those with the thermostat at 195°K., and finally those with the thermostat at 273°K., the substance being cooled down to the thermostat temperature from above before the start of each run.

The method of calculation differs from that of Paper I in one point; in this research actual experimental heating times, averaged[11] over the several runs of a set, were used for the calculation of the heat capacities, instead of the smoothed-curve values described in Paper I.

Calibration and Testing.—The temperature of the substance in the can was measured by means of a copper-constantan thermocouple.[12] This couple was calibrated by checking its e. m. f. against the tables of Southard and Andrews[13] and Smith[14] at several well-known "fixed points" (the boiling point of oxygen, the sublimation point of carbon dioxide, the freezing point of mercury, the ice point, the transition point of sodium sulfate decahydrate and the steam point). The temperature measurements are estimated to be correct to ±0.2° below 200°K. and to ±0.1° above 200°K.[15]

The heat capacity values of the standard substance, potassium chloride, are discussed in Paper I.

The operation of the calorimeter was checked with ammonium chloride and potassium chlorate, the heat capacities of which had been determined with high accuracy by absolute methods. For ammonium chloride the average deviation of the results of this research from those of Simon[16] was 1.5% over the temperature range 100 to 290°, excluding the transition region 237–249°K. They are considerably below Simon's results above 270°K., but agree with those of Paper I in this region. The transition temperature, 242.6°K., and the heat of transition, 272 cal./mole, also agree well with the values reported in Paper I.

The high temperature heat capacity results of this research on ammonium chloride may be represented by the formula $C_p = 9.8 + 0.0335\,T$ from 273 to 353°K., with an average deviation of 0.5%.

For potassium chlorate the average deviation of the results of this research from those of Latimer, Schutz and Hicks[17] from 100 to 285°K. was only 0.5%, the higher accuracy of these measurements being attributed chiefly to the fact that the heating intervals were timed to 0.2 second rather than to one second as in all other cases. The formula $C_p = 14.39 + 0.0322\,T$ holds for the present results on potassium chlorate from 273 to 373°K. with an average deviation of 0.25%.

The results for both salts are in excellent agreement with the high temperature measurements of Ewald[18] and Brönsted.[19]

The accuracy of the heat capacity measurements may be further checked in certain temperature regions by two sets of measurements on the same sample with different outer thermostat media, as mentioned before. The average difference between the heat capacity values of the two sets, compared in this way, amounted to 1.7% for ammonium chloride and 0.8% for potassium chlorate. These are of the same order of magnitude as the previously cited

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[9] Gore, *Proc. Roy. Soc.* (London), **37**, 283 (1884).

[10] These methods of preparation and purification are given by Thompson, *Bur. Standards J. Research*, **6**, 1051 (1931).

[11] Such averaging of heating times can be done with the heat conduction calorimeter because the temperature intervals over which such times are measured are the same in all runs.

[12] See Paper I for the source of the constantan wire used.

[13] Southard and Andrews, *J. Franklin Inst.*, **207**, 323 (1929).

[14] R. H. Smith, Dissertation, The Johns Hopkins University, 1930.

[15] 0°C. was taken as 273.10°K.

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

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

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

[19] Brönsted, *Z. Elektrochem.*, **18**, 714 (1912).

average deviations from the absolute measurements of 1.5% and 0.5%, respectively. They are due largely to consistent rather than erratic individual differences between the two sets of measurements.

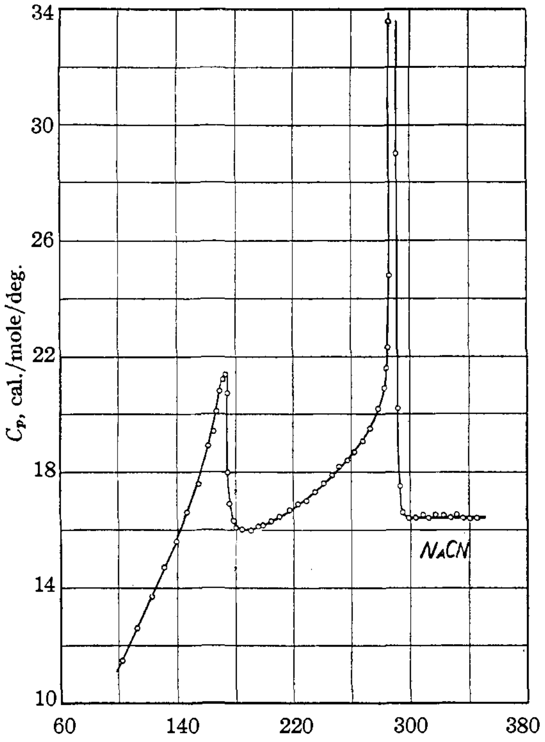

Fig. 1.—Heat capacity of sodium cyanide in calories per mole per degree.

Sodium and Potassium Cyanides.—The experimental heat capacities of sodium and potassium cyanides over the range 100 to 345°K. are given in Tables I–III, and are plotted graphically in Figs. 1 and 2. They represent average values for all measurements made at a given temperature. For sodium cyanide seven runs were made with the outer thermostat at 77°K., five runs with the outer thermostat at 195°K. (to be referred to later as Set I), and two runs with the outer thermostat at 273°K. (Set II), all with a sample weighing 8.13 g. In addition, two runs were made with the thermostat at 195°K. on a sample weighing 8.09 g. (Set III), and three runs were made with the thermostat at 273°K. on a sample weighing 7.14 g. (Set IV). Each set was weighted equally in determining the final average value quoted for a given temperature. For potassium cyanide only one sample of 5.96 g. was used and two runs were made with each of the three media in the outer thermostat.

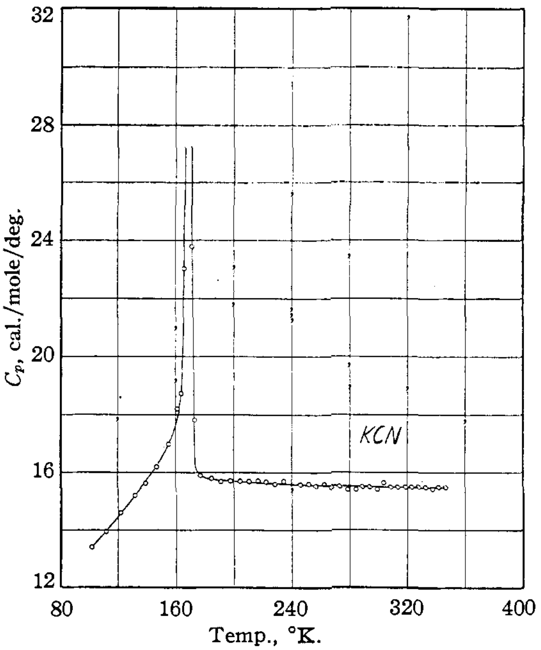

Fig. 2.—Heat capacity of potassium cyanide in calories per mole per degree.

Results

The transition reported for sodium cyanide by Bijvoet and Verweel[7] near 288°K. was confirmed, and an additional, more gradual, transition was found at about 172°K. A single transition was found for potassium cyanide at 168°K. Table I contains the heat capacity of both sodium and potassium cyanides at all temperatures excluding those in the vicinity of the transitions. Tables II and III contain the heat capacities of sodium and potassium cyanides, respectively, in the transition regions of temperature. ΔT is the temperature increment for which the mean heat capacity is given, T being the mean temperature of the increment. The transition temperatures,[20] estimated heats of transition,[21] and the ranges of

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[20] Cooling observations of the cyanides were also made through the transition regions. The transition temperature of potassium cyanide was found to be 4.0° lower on cooling than on warming, and the upper transition temperature of sodium cyanide was similarly 6.0° lower. The lowering of the transition temperature of 6.0° for sodium cyanide was the same when the outer thermostat was at 273°K. as when it was at 195°K., even though the cooling rate at the transition was 6 times as rapid in the latter case as it was in the former. The lower transition of sodium cyanide could not be detected at all on cooling to below 155°K., although the cooling rate was the same as that of potassium cyanide, the transition of which was detected. These observations suggest a hysteresis effect of supercooling at the transition temperatures in each case.

[21] See Paper I for method of calculation. The values of the heats of transition of the cyanides are much more uncertain than those of the ammonium salts because of the greater arbitrariness in the selection of the "normal" curve, and are therefore given only approximately in Table IV.

temperature for the extrapolations used in estimating these heats, are given in Table IV.

TABLE I

HEAT CAPACITY OF SODIUM AND POTASSIUM CYANIDES

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

T, °K.	C_p, cal./mole/deg. NaCN	KCN	T, °K.	C_p, cal./mole/deg. NaCN	KCN
101.6	11,5	13.4	251.5	18.2	15.6
111.7	12.6	13.9	257.0	18.4	15.5
121.3	13.7	14.6	262.4	18.7	15.6
130.3	14.7	15.2	267.7	19.1	15.5
138.9	15.6	15.6	273.1	19.5	15.5
147.2	16.6	16.2	278.4	20.2	15.4
155.1	17.6	17.0	283.6		15.4
			288.6		15.5
177.3		15.9	293.7		15.5
184.2	16.0	15.8	298.6	16.4	15.4
191.1	16.0	15.7	303.5	16.4	15.6
197.7	16.2	15.7	308.4	16.5	15.5
204.2	16.3	15.7	313.2	16.4	15.5
210.5	16.5	15.7	318.0	16.5	15.5
216.7	16.7	15.7	322.7	16.5	15.5
222.7	16.9	15.7	327.4	16.4	15.5
228.7	17.0	15.6	332.0	16.5	15.5
234.5	17.3	15.7	336.7	16.4	15.4
240.3	17.6	15.6	341.3	16.4	15.5
245.9	17.9	15.6	345.8	16.4	15.5

TABLE II

HEAT CAPACITY OF SODIUM CYANIDE, TRANSITION REGIONS

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
160.9	3.77	18.9	287.3	0.51	71
164.6	3.71	19.4	287.7	.25	140
167.4	1.83	20.1	288.0	.25	210
169.2	1.82	20.8	288.2	.25	310
170.9	1.45	21.2	288.5	.25	370
172.3	1.44	21.4	288.7	.25	340
173.8	1.43	20.7	289.0	.25	270
175.2	1.42	18.0	289.2	.25	190
176.6	1.42	16.9	289.5	.25	150
178.2	1.76	16.3	289.9	.50	101
179.8	1.74	16.1	290.4	.50	64
			290.9	.50	42
282.2	2.57	20.9	291.4	.50	29.0
284.2	1.28	21.6	292.1	1.00	20.2
285.4	1.27	22.3	293.1	1.00	17.5
286.3	0.51	24.8	294.9	2.49	16.6
286.8	.51	33.6			

TABLE III

HEAT CAPACITY OF POTASSIUM CYANIDE, TRANSITION REGION

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
160.9	3.77	18.2	168.5	0.37	124
163.7	1.87	18.7	168.9	.36	111
165.6	1.85	23.0	169.2	.36	84
166.8	0.74	48.8	169.8	.73	56.6
167.4	.37	84	171.0	1.81	23.8
167.8	.37	114	172.9	1.79	17.8
168.1	.37	123			

TABLE IV

TRANSITION DATA: SODIUM AND POTASSIUM CYANIDES

	Transition temp., °K.[20]	Heat of transition,[21] cal./mole	Range of extrapolation, °K.
NaCN	172.1 ± 0.5	150	100–190
	288.5 ± 0.3	700	190–300
KCN	168.3 ± 0.4	300	115–180

The accuracy of the heat capacity values may be judged from the agreement of the data obtained in those temperature regions in which two outer thermostat media were used. For sodium cyanide the average deviation from the mean in these temperature regions was about 1%; for potassium cyanide it was 0.5%. The maximum error of the heat capacity values is estimated at ±3% for sodium cyanide and at ±2% for potassium cyanide, except in the transition regions where it is higher. At the temperature of largest heat capacity, the maximum error, based upon uncertainties in the measurements of the heating times and of the temperature increment ΔT, is estimated at ±8% for the transition of sodium cyanide at 172°K., and at ±20% for the sodium cyanide transition at 288.5°K. and for the single transition of potassium cyanide. At temperatures other than the peak temperature of the transition, these errors would, of course, be lower than at the peak, but higher than the "normal" values. Variations in the temperature scale would also contribute an additional error which would be appreciable but difficult to estimate in the transition region. However, measurements of the transition temperature of ammonium chloride showed no irregularities of this sort of more than 0.05°.

For the single transition of potassium cyanide and the transition of sodium cyanide at 172°K., the experimental data show the maximum error of the heat capacity results to be well within the limits just described. For the transition of sodium cyanide at 288.5°K., however, deviations of individual heat capacity results from the mean are much larger than would be expected, amounting to over 40% in certain cases. Accordingly the heat capacity results given for the range 283–294°K. are of value only in showing the qualitative behavior of the heat capacity in this temperature region.

These irregularities in heat capacity values for sodium cyanide naturally were reflected in variations in the transition temperature, or temperature of highest heat capacity. In the case of those runs in which the sample was cooled to 195°K., previously described as Set I and Set III, the first run of each set gave a transition temperature 0.15–0.25° above the average value of 288.5°K.; all subsequent runs gave a transition temperature of 288.5°K. In the case of those runs in which the sample was cooled only to 273°K., Set II showed no evidence of a trend, but Set IV showed a trend in transition temperature from 288.35 to 288.45° in three successive runs. These variations seem to take the form of an apparent trend toward an equilibrium temperature of 288.5°.

Despite these irregularities in the heat capacity behavior of sodium cyanide in this transition region, the average experimental value of 767 cal./mole for the increase in heat content of this substance from 283.5 to 293.6°K. has a maximum deviation from the mean of only 9 cal. for all runs.

Discussion

It has been found possible to make certain deductions as to the freedom of rotational motion of the cyanide ions in sodium and potassium cyanides from calculations of the type of Eucken.[3] This type of calculation, which is based in part on experimental and in part on empirical data, rests on the approximation that the total heat capacity of a solid (C_p) can be regarded as the sum of terms due to the lattice (C_L), to the rotational motion of groups (C_R), to internal vibration of groups (C_{vib}), and to expansion ($C_p - C_v$). If all these terms except C_R are known as functions of the temperature, then this latter term may be evaluated as a function of the temperature, and the analysis which has just been discussed can be applied.

The exact application of Eucken's type of analysis to the cyanides is impossible because of the lack of the necessary data with which to determine C_L and $C_p - C_v$. However, these quantities are known for the alkali halides, which have the same structure as the cyanides, and it has been possible on this basis to make empirical estimates of the rotational heat capacity of the cyanides at various temperatures.

In estimating C_L for the cyanides, values of the Debye θ equal to those of the corresponding chlorides have been selected: 280[22] for sodium cyanide, and 210[23] for potassium cyanide as an average value between 200 and 350°K. Comparing the two sets of salts, the lowering of the lattice vibration frequency by replacing a chloride ion with a larger[24] cyanide ion opposes and may be assumed to balance roughly the increase in vibration frequency due to the smaller weight of the cyanide ion. At any rate, C_L is not very sensitive to the choice of Debye θ at higher temperatures.

For the chlorides and bromides of sodium and potassium, the quantity $C_p - C_v$ varies from 0.45 to 0.6 cal./mole/deg. at 273°K.,[25] the potassium salt having in each case a smaller value of $C_p - C_v$ than the corresponding sodium salt. For ammonium chloride $C_p - C_v$ at 273°K. lies between 0.6 and 0.8 cal./mole/deg.[26]

The values 0.7 for potassium cyanide and 0.8 for sodium cyanide have accordingly been selected for $C_p - C_v$ at 273°K., and the estimations at other temperatures made by means of the formula $C_p - C_v = AC_p^2T$. The constant A is 1.1×10^{-5} cal.$^{-1}$ for both salts. Because of the possibility that this formula might not hold in a transition region, calculations were made for the cyanides only at temperatures 25° or more removed from transitions, and the value $C_p = 16.5$ cal./mole at 273°K. was used for sodium cyanide in evaluating the constant A, this being the "normal" value employed in the estimation of the heat of the transition at 288.5°K.

The vibrational contribution of the cyanide ion to the heat capacity is negligibly small due to the high vibration frequency of the ion ($\bar{\nu} = 2085$ cm.$^{-1}$).[27]

The results of the calculation of the rotational heat capacity of sodium and potassium cyanides appear in Table V. It is assumed that the elastic properties of orthorhombic sodium cyanide below 288.5°K. are sufficiently like those of the cubic form to permit the use of the same approxima-

TABLE V

ROTATIONAL HEAT CAPACITY C_R OF THE CYANIDES

T, °K.	Total C_p cal./mole/deg.	C_L $6D(\theta/T)$	$C_p - C_v$	C_R
		NaCN		
200	16.2	10.8	0.6	4.8
240	17.6	11.2	.8	5.6
320	16.4	11.5	.9	4.0
350	16.4	11.6	1.0	3.8
		KCN		
200	15.7	11.3	0.5	3.9
240	15.6	11.5	.6	3.5
273	15.5	11.6	.7	3.2
350	15.5	11.7	.9	2.9

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(22) Schrödinger, *Physik. Z.*, **20**, 450 (1919).

(23) See Paper I for a discussion of the high temperature behavior of θ for potassium chloride.

(24) The radius of the cyanide ion in the cubic alkali cyanides is about 1.93 Å. (ref. 4), while that of the chloride ion is 1.81 Å. (Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939).

(25) These quantities were calculated from the densities, coefficients of expansion, and compressibilities given in "International Critical Tables," Vol. III, pp. 43, 50.

(26) Based on the density data given in "I. C. T.," Vol. I, p. 43, the compressibility data of Bridgmann, *Phys. Rev.*, **38**, 182 (1931), and for the lower figure on the expansion coefficient found by Lawson, *Phys. Rev.* **57**, 417 (1940); for the higher figure on the expansion coefficient found by Simon and Bergmann, *Z. physik. Chem.*, **B8**, 255 (1930).

(27) (a) Kohlrausch, "Der Smekal-Raman Effekt," J. Springer, Berlin, 1931; (b) Gordy and Williams, *J. Chem. Phys.*, **3**, 664 (1935).

tions. The maximum error in C_R is estimated at 1.0 cal./mole/deg.

The decrease of C_R with increasing temperature in the cubic forms of both salts above their uppermost transitions is similar to that found by Eucken for many substances, and supports the hypothesis that the cyanide ions are actually rotating in these salts at these temperatures. Teller and Weigert[28] have furthermore shown that the heat capacity of a hindered rotator can rise to a maximum value of greater than R cal./mole per rotational degree of freedom (the classical value for a completely hindered rotator) and then fall off with increasing temperature, approaching at high temperatures the classical value of $^1/_2\ R$ cal./mole per degree of freedom, the value for a free rotator.

The rotation is not free in either salt at any temperature reached in this research, since in all instances excepting potassium cyanide at 350°K. C_R is greater than 2 cal./mole/deg. even within the limits of error of the calculation. Even here the continuing decrease of C_R with increasing temperature makes it highly probable that there is still some hindrance to rotation, since the drop in C_R with increasing temperature is almost certainly real even though the absolute values may be considerably in error. The effect of the potential barrier is especially pronounced just above the transitions as shown by the high values of C_R, truly free rotation apparently being approached only at high temperatures.

The calculations also indicate very little possibility of rotation of the cyanide in sodium cyanide at or above 200°K., C_R being 4 cal./mole/deg. or larger, and increasing as the upper transition approaches.

The most satisfactory viewpoint on the significance of the two transitions of sodium cyanide at 172 and at 288.5°K. is that they are analogous to the two transitions of ammonium chloride at 243 and 457°K., respectively. The analysis of the heat capacity values shows in each case[29] that the lower transition does not result in relaxation of the restriction on rotation, but that the upper one probably does. The relative sharpness and large heat effect further support the X-ray evidence that a change in crystal structure is associated with the upper transition of sodium cyanide.

The most recent theoretical papers[30] regard many of these so-called "rotational transitions" as actually transformations from order to disorder in the orientations of the molecules or ions in the solid. Menzies and Mills[31] and Lawson[26] have discussed the transition of ammonium chloride at 243°K. in terms of such a transformation. The gradual transition of sodium cyanide at 172°K. probably can be interpreted most satisfactorily in terms of such an order–disorder transformation in the orientations of the cyanide ions in the lattice. It is interesting to note here that Bijvoet and Verweel[7] found the same orthorhombic structure at 143 and 263°K., but they report an unusual contraction of the 6-axis of the unit cell on warming from the lower to the higher temperature. This contraction, if real, is undoubtedly associated with the transition at 172°K.

The nature of the transition of potassium cyanide at 168°K. cannot be discussed adequately on the basis of the present research.

Summary

1. The heat capacities of sodium and potassium cyanides have been measured from 100 to 345°K. by means of a calibrated heat conduction calorimeter.

2. Sodium cyanide was found to exhibit two regions of anomalous heat capacity with maxima at 172.1 ± 0.5°K. and 288.5 ± 0.3°K., respectively. For potassium cyanide one such region was found with a maximum at 168.3 ± 0.4°K. The heats of these "transitions" have been estimated.

3. Certain anomalies were found in the behavior of sodium cyanide in the vicinity of its upper transition which may be associated with non-equilibrium phenomena.

4. That portion of the heat capacity due to the rotation of the cyanide ion was estimated for both salts. These calculations indicate that there is partially restricted rotation of the cyanide ions in the cubic modifications of both salts, and that the hindrance to rotation diminishes only gradually with increasing temperature. They indicate highly restricted rotation in the low temperature modification of sodium cyanide in the temperature region between the two transitions.

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(28) Teller and Weigert, *Nachr. Ges. Wiss. Göttingen, Math. phys. Klasse*, 218 (1933).

(29) See Eucken, ref. 3, for the analysis of the heat capacity of ammonium chloride.

(30) Frenkel, *Acta Physicochimica U. S. S. R.*, **3**, 23 (1935); Kirkwood, *J. Chem. Phys.*, **8**, 205 (1940).

(31) Menzies and Mills, *Proc. Roy. Soc.* (London), **A148**, 407 (1935).