

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

**Phase Transitions. I. The Heat Capacity of Nickel Nitrate Hexammoniate from 54 to 300°K. The Transition at 243°K.**BY EARL A. LONG AND FRED C. TOETTCHER<sup>1</sup>

The crystal structure of nickel nitrate hexammoniate was first investigated by Wyckoff,<sup>2</sup> who assigned to it a fluorite type structure with paramorphic hemihedry. Wyckoff was unable to determine accurately the positions of the nitrate groups; later work on other nitrates by Kracek, *et al.*,<sup>3</sup> indicates that his proposed structure is probably unsatisfactory, and suggests that the nitrate groups are rotating in the crystal.

Yü<sup>4</sup> has recently re-investigated the crystal structure of this compound over the temperature range 80 to 300°K., with the technique of both powder and oscillation photographs. His work indicates that nickel nitrate hexammoniate probably has holohedral Laue symmetry, and that the nitrate groups carry out pronounced torsional oscillations at temperatures above 170°K. Yü also reports a possible transition at *ca.* 80°K.

We have measured the heat capacity curve of the substance from 54 to 300°K., in order to obtain more definite information concerning the behavior of the nitrate groups in the crystal lattice.

**Experimental**

**Apparatus.**—The measurements from 85 to 300°K. were made with a modified Nernst vacuum calorimeter, essentially as developed by Giauque and co-workers.<sup>5,6</sup> The copper calorimeter was fitted with twelve radial vanes to promote rapid thermal equilibrium, and had an externally wound gold resistance thermometer of 214 ohms resistance at 300°K.

Temperatures below 85°K. were attained with a condensation ring calorimeter, as described by Clusius and Harteck.<sup>7</sup> For these measurements, we used a calorimeter fitted with a helical-wound strain-free platinum resistance thermometer.<sup>8</sup> Both thermometers were calibrated in terms of a standard copper-constantan thermocouple, which had itself been calibrated against a helium gas thermometer by one of us, and had later been standardized for us by the U. S. Bureau of Standards.<sup>9</sup> The temperatures recorded in this paper are believed accurate to 0.05°, in an absolute sense.

The energy input for the calorimetric measurements was timed with an accurate signalling chronometer, which was kindly made available to us by Professor E. S. Haynes of the Department of Astronomy in this University. Hand-control switches were used, resulting in an over-all timing accuracy of 0.1 second. Electrical measurements were made on a White double potentiometer and a Leeds and Northrup microvolt potentiometer.

The details of the methods used and the corrections to be applied have been adequately described by Giauque.<sup>5,6</sup>

**Preparation and Analysis of Nickel Nitrate Hexammoniate.**—The compound was prepared by adding concentrated ammonium hydroxide in excess to a cold concentrated solution of nickel nitrate, according to the method of Wyckoff<sup>1</sup> and King, Cruse and Angell.<sup>10</sup> Recrystallized Mallinckrodt analytical reagent nickel nitrate and C. P. ammonium hydroxide were used. The resulting compound was washed with alcohol and ether, and was then kept over soda-lime at 4°. The salt loses ammonia at room temperatures, but can be stored indefinitely at 4° without decomposition.

Ignition to nickelous oxide yielded 26.27% Ni; theoretical, 26.21%. Titration for ammonia content gave 35.45%; theoretical, 35.87%. The density, from pycnometer measurements, was 1.461; Wyckoff reported 1.46, from a Westphal balance determination.

The filled calorimeter was carefully kept below the ice-point at all times, except for the final measurements above 260°K., in order to prevent decomposition of the sample. Analyses made immediately after the removal of the sample indicated no decomposition had occurred under these conditions, even over an interval of several months.

**Cooling Curve.**—A cooling curve measurement showed a pronounced break, starting at 246°K., with a minimum in the cooling rate at 239°K. There was no indication of a strictly isothermal effect. The rate of cooling was observed to 70°K., but no indication of a lower transition was found. Beevers and Jensen,<sup>11</sup> from similar measurements, located the transition at 244.5°K., but also found no evidence of the lower transition predicted by Yü. However, our heat capacity data later revealed anomalous thermal behavior in the solid below 80°K., of a magnitude too small for detection by a cooling curve. The discrepancy between the transition temperatures reported by Beevers and Jensen and ourselves, along with the more accurate value which we obtain from heat capacity data, suggest that the transition exhibits hysteresis.

**Heat Capacity Measurements.**—The heat capacity data are given in Table I. For the calculation of energy, 1.00041 absolute joules were taken equal to one International joule, and 4.1852 absolute joules to one calorie (15°). 0.1235 mole was used for the measurements from 54 to 85°; 0.1156 mole for those above 85°K. The data are shown graphically in Figs. 1 and 2.

(10) King, Cruse and Angell, *J. Chem. Soc.*, 2928 (1932).(11) Beevers and Jensen, *Trans. Faraday Soc.*, 84, 1478 (1938).

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(2) Wyckoff, *THIS JOURNAL*, 44, 1260 (1922).(3) Kracek, Hendricks and Posnjak, *Nature*, 128, 410 (1931).(4) Yü, *ibid.*, 141, 158 (1938).(5) Giauque and Wiebe, *THIS JOURNAL*, 50, 101 (1928).(6) Giauque and Johnston, *ibid.*, 51, 2300 (1929).(7) Clusius and Harteck, *Z. physik. Chem.*, B134, 243 (1928).(8) Cf. Meyers, *U. S. Bur. Sids. J. Res.*, 9, 807 (1932).

(9) We are much indebted to Dr. F. G. Brickwedde for this accurate calibration.

TABLE I

HEAT CAPACITY OF NICKEL NITRATE HEXAMMONIATE  
Molecular wt., 284.90; 0°C. = 273.16°K.

| $T_1$ ,<br>°K. | $\Delta T$ | $C_p$ ,<br>cal./-<br>mole/-<br>deg. | Series | $T_1$ ,<br>°K. | $\Delta T$ | $C_p$ ,<br>cal./-<br>mole/-<br>deg. |
|----------------|------------|-------------------------------------|--------|----------------|------------|-------------------------------------|
| 54.57          | 0.938      | 32.72                               | V      | 146.06         | 5.739      | 67.81                               |
| 55.96          | 2.118      | 33.78                               | V      | 150.22         | 6.177      | 68.70                               |
| 58.48          | 2.590      | 34.81                               | V      | 156.33         | 5.827      | 71.09                               |
| 60.48          | 2.131      | 35.47                               | I      | 163.02         | 5.763      | 73.08                               |
| 61.10          | 2.522      | 35.81                               | V      | 168.21         | 6.177      | 74.69                               |
| 62.81          | 2.608      | 36.69                               | I      | 176.88         | 6.552      | 77.42                               |
| 63.62          | 2.438      | 37.41                               | V      | 183.33         | 6.244      | 79.37                               |
| 66.47          | 3.095      | 38.67                               | I      | 189.54         | 6.008      | 80.71                               |
| 67.97          | 3.600      | 39.52                               | I      | 195.49         | 5.790      | 82.16                               |
| 72.08          | 3.357      | 41.67                               | I      | 201.56         | 6.300      | 83.88                               |
| 74.41          | 2.219      | 42.89                               | II     | 208.04         | 6.516      | 85.69                               |
| 75.25          | 2.945      | 43.04                               | I      | 212.99         | 6.555      | 87.80                               |
| 76.59          | 2.184      | 42.80                               | II     | 216.45         | 6.022      | 88.09                               |
| 78.15          | 2.865      | 43.28                               | I      | 222.37         | 5.764      | 90.52                               |
| 80.46          | 1.103      | 43.25                               | II     | 227.96         | 5.536      | 92.68                               |
| 80.65          | 3.340      | 43.31                               | I      | 233.79         | 5.848      | 98.10                               |
| 81.57          | 1.091      | 43.99                               | II     | 239.25         | 4.610      | 107                                 |
| 82.69          | 1.083      | 44.33                               | II     | 241.87         | 0.905      | 228.9                               |
| 83.67          | 2.652      | 44.58                               | I      | 242.56         | .293       | 281.8                               |
| 83.77          | 1.074      | 44.90                               | II     | 242.90         | .290       | 1067                                |
| 86.43          | 2.780      | 46.08                               | I      | 243.21         | .278       | 1271                                |
| 89.32          | 2.888      | 47.02                               | I      | 243.61         | .338       | 1019                                |
| 92.32          | 4.267      | 48.10                               |        | 244.40         | 1.099      | 220.1                               |
| 95.35          | 3.083      | 49.39                               |        | 246.07         | 2.079      | 93.56                               |
| 98.50          | 3.173      | 50.46                               |        | 250.90         | 5.687      | 90.30                               |
| 102.74         | 4.819      | 52.12                               |        | 254.80         | 5.569      | 90.89                               |
| 107.84         | 5.596      | 54.49                               |        | 257.37         | 5.501      | 90.46                               |
| 113.27         | 5.205      | 56.89                               |        | 260.26         | 4.797      | 93.00                               |
| 116.17         | 5.289      | 57.67                               |        | 265.17         | 4.688      | 94.96                               |
| 121.96         | 6.104      | 59.95                               |        | 269.78         | 4.636      | 94.11                               |
| 127.90         | 5.660      | 61.86                               |        | 275.20         | 4.516      | 94.53                               |
| 133.42         | 4.997      | 63.94                               |        | 282.96         | 1.713      | 95.50                               |
| 138.36         | 4.720      | 65.44                               |        | 286.62         | 4.734      | 95.56                               |
| 140.09         | 6.054      | 65.76                               |        | 292.52         | 5.998      | 95.96                               |
| 145.21         | 5.480      | 67.62                               |        | 295.51         | 1.620      | 95.89                               |

The heat capacity curve shows the existence of a gradual

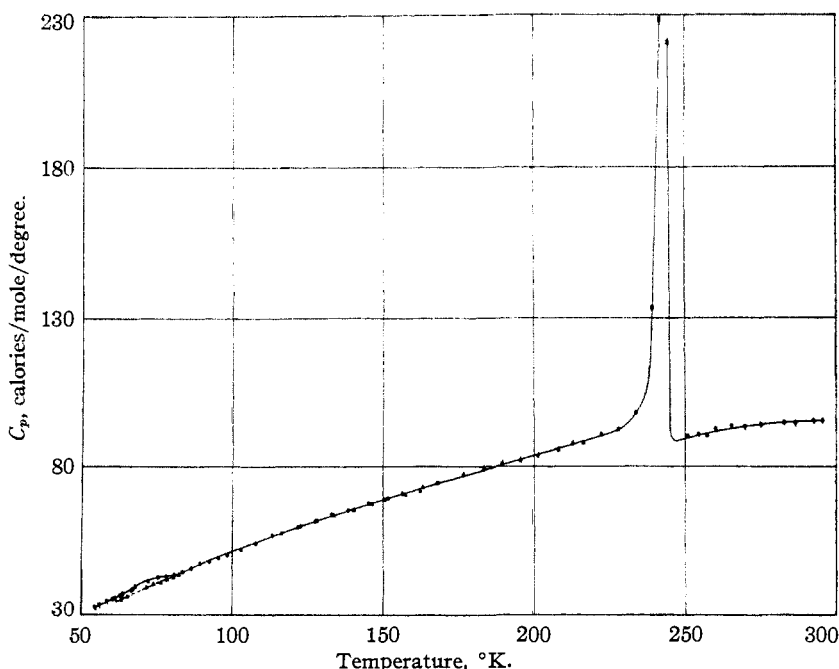


Fig. 1.—Heat capacity of nickel nitrate hexammoniate, 54–300°K.

transition extending from 173 to 247°K., with abnormal  $C_p$  values occurring around 173°K., and increasing to a very high maximum at 243.3°K. In addition, there is a region of anomalous behavior below 80°K.; unfortunately, we were unable to investigate this phenomenon at sufficiently low temperatures, as we do not yet have liquid hydrogen available.

**The Transition Region, 173 to 247°K.**—In this region, the heat capacities depend on the thermal history of the sample. In our first measurements, taken without special precautions in cooling the sample, we obtained unreproducible values of the heat capacity. The values were always too high, often by as much as fifteen per cent. The behavior was just that to be expected if the 243° transition were supercooled. Accordingly, we cooled the sample very rapidly through the transition, to 80°K., maintained it there for several days, and then repeated the measurements. As expected, the values were again too high. The sample was then maintained at 210°K. for twelve hours. After this treatment, the heat capacities dropped to their equilibrium values. In another experiment, the sample was cooled slowly through the transition, and was then held at 235°K. for several hours prior to cooling to 80°K. This procedure also yielded normal heat capacity data. Several additional experiments indicated that these effects could be repeated at will. It is concluded, therefore, that the substance can be supercooled easily, the rate of transformation being inappreciable at temperatures much below 170°K.

We attempted to measure the rate of transformation by observing the warming rate of the calorimeter at various temperatures, with negligible heat leak from the surroundings. The expected warming rate at 210°K. was calculated to approximate 0.0003° per minute, too small for accurate observation. However, we did detect warming rates of that order of magnitude, and were able to make similar observations even at the peak of the curve, at 243.3°K., where the heat capacity is at a maximum. The existence of this slight warming rate in the peak region is of some qualitative significance, indicating that perhaps there is no isothermal absorption of energy in the peak. This argument is, however, weakened by the heat capacity data in the region of highest energy absorption, which always gave evidence of poor thermal equilibrium.

The data given in Table I and Fig. 1 represent true equilibrium heat capacities; no measurements on the supercooled form are included.

**Heat of Transition.**—The nature of the transition precludes an accurate evaluation of  $\int C_p dT$  in the transition

region by means of heat capacity runs over small temperature intervals. For this reason,  $\int C_p dT$  was determined by measuring the total heat input over the temperature interval 227 to 247°K., and then deducting the "normal"  $\int C_p dT$  obtained by interpolating the "normal" heat capacity curve through this region. We also included a graphical integration of the excess heat effect from 173 to 227°K. Corrections for heat interchange during energy input were evaluated graphically, using an empirically determined Newton's law constant.

TABLE II  
HEAT OF TRANSITION, 173 TO 247°K.

|   |                |
|---|----------------|
| Corrected heat input per mole, 227-247° | I 3526         |
|   | II 3507        |
|   | III 3525       |
| Average                                 | 3519 = 12 cal. |

|  |                    |
|--|--------------------|
| $\int C_p dT$ , "normal" $C_p$ curve, 227-247° | 1784               |
| "Excess" $\int C_p dT$ , 227-247°              | 1735               |
| "Excess" $\int C_p dT$ , 173-227°              | 83                 |
| Heat of transition, 173-247°                   | 1818 cal. per mole |

**Entropy of Transition.**—The usual method of obtaining entropies by graphical evaluation of  $\int C_p d \ln T$  is not applicable to this case because of the uncertainty in evaluating areas under the peak. The calculation was made by integrating graphically over the region of "excess" heat capacity up to the highest well-defined point on the curve, and then dividing the remaining abnormal heat effect by the average temperature over that interval. The resulting entropy of transition is  $7.65 \pm 0.5$  E. U. This value is concerned with the transition only, and should not be used in calculating the *total* entropy of the compound. The rather large limit of error is caused by difficulty in establishing the "normal"  $C_p$  curve between 173 and 247°K.

### Discussion

It seems fairly certain that the application of Pauling's original theory<sup>12</sup> of the transition from libration to rotation will fail to explain this relatively high entropy of transition. We thought at first<sup>13</sup> that the transition could be correlated with oscillations of both the nitrate and ammonia groups, but a careful consideration of the crystal structure makes this extremely unlikely. Beevers and Jensen<sup>11</sup> found no evidence of transitions in nickel chloride hexammoniate, which has a similar

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

(13) Cf. Long and Toettcher, *J. Chem. Phys.*, **8**, 504 (1940).

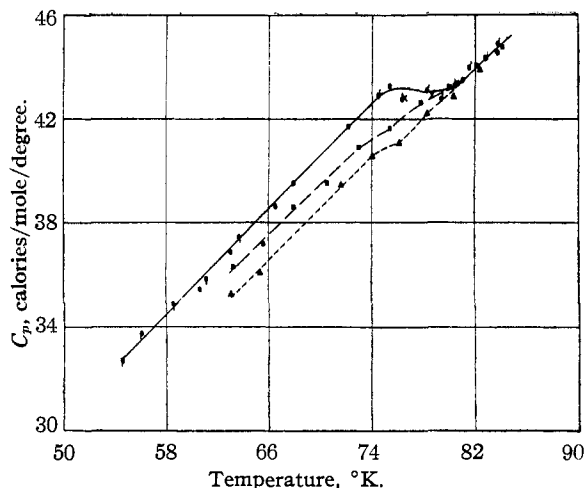


Fig. 2.—Heat capacity of nickel nitrate hexammoniate, 54-85°K.: ●, Series I; ●, Series II; ×, Series III; ■, Series IV; ●, Series V; ▲, Series VI.

crystal structure. However, Ziegler<sup>14</sup> has reported a lambda-type transition in  $\text{Co}(\text{NH}_3)_6\text{I}_3$ , which must presumably be attributed to the ammonia groups. The heat of transition is much lower (420 cal./mole).  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  and  $\text{Co}(\text{NH}_3)_6\text{I}_2$  show no transitions between 100 and 300°K. It would be interesting, therefore, to examine  $\text{NiI}_2 \cdot 6\text{NH}_3$  for possible transitions; Yü's X-ray data indicate normal behavior for the  $\text{Ni}(\text{NH}_3)_6^{++}$  ions in the nitrate.

Any attempt to correlate an experimental entropy with the process occurring in such a transition must necessarily be inaccurate: (1) because of the practical difficulty in assigning a "normal" heat capacity curve, and (2) because the whole character of the lattice frequencies is undoubtedly changed after the onset of such a cataclysmic event in the crystal. The following is presented as a reasonable, but not conclusive, explanation of the transition.

Let us assume, with Yü, that the nitrate groups are oscillating in the crystal, and, in addition, assume that the transition involves a change from order to disorder in the orientation of the nitrate groups with respect to the crystal axes. Below the transition, each nitrate will be oriented with respect to a single axis only; above the transition it can line up in any one of a number of orientations. Two possible values for the entropy then arise. If Wyckoff's assignment of paramorphic hemihedral symmetry is correct, then we have four three-fold axes of symmetry. A nitrate group can presumably line up on either side of a

(14) Ziegler, *THIS JOURNAL*, **63**, 2700 (1941).

symmetry axis, and therefore we have  $k \ln 8$  as the entropy of disorder per nitrate, or  $2R \ln 8 = 8.24$  E. U. per mole. On the other hand, following Yü's assignment of holohedral Laue symmetry, we have three four-fold axes of symmetry, and the entropy becomes  $2R \ln 6 = 7.12$  E. U. per mole. The experimental value of  $7.65 \pm 0.5$  E. U. is in agreement with both interpretations, and thus the question of symmetry assignment does not affect the argument. The agreement is about as good as could be expected, in view of the limitations of the comparison.

**The Temperature Region 54 to 80°K.**—The measurements below 80° also revealed anomalous heat capacities which depended on the thermal history of the sample. These data, shown in Fig. 2, were obtained as follows. In Series I, the sample was held at 210°K. for fifteen hours; it was then cooled to 80° and held for twelve hours before the final rapid cooling to 57°K. The data for this series gave heat capacities about five per cent. high, as compared to a curve extrapolated from 85° (see Fig. 1). In Series II and III, with essentially the same treatment, similar heat capacities were measured. Series IV was run with incomplete transformation from the 243° transition, but with very slow cooling from 83 to 73°K. Below 81°, these points are consistently lower than those of the preceding measurements. Series V was run after complete transformation of the upper transition, and then very slow cooling to 54°K.; these points agreed with those of Series I, II and III. Finally, in Series VI, the sample was cooled very rapidly through the 243° transition, to ensure the maximum supercooling effect, and was then held at 85°K. for thirty-four hours before cooling to 54°. The points of this series were the lowest measured, falling almost on the curve which one would normally extrapolate from the higher temperature data (see broken curve in Fig. 1).

The measurements of Series I, II and V are included in Table I; those of Series IV and VI are given in Table III. It is obvious from these data that complete supercooling of the 243° transi-

tion would have the effect of eliminating the anomalous behavior below 80°K., thus leading to non-equilibrium heat capacity data. The measurements of Series I, II and V should therefore represent the true heat capacity curve below 80°K.

TABLE III  
MEASUREMENTS ON SUPERCOOLED FORM

| $T_i$<br>°K.                     | $\Delta T$ | $C_p$ ,<br>cal./mole,<br>deg. | $T_i$<br>°K.           | $\Delta T$ | $C_p$ ,<br>cal./mole,<br>deg. |
|----------------------------------|------------|-------------------------------|------------------------|------------|-------------------------------|
| Series IV, partially supercooled |            |                               | Series VI, supercooled |            |                               |
| 63.12                            | 2.302      | 36.16                         | 63.06                  | 2.519      | 35.26                         |
| 65.47                            | 2.453      | 37.20                         | 65.28                  | 2.481      | 36.10                         |
| 67.93                            | 2.608      | 38.59                         | 71.64                  | 2.293      | 39.51                         |
| 70.50                            | 2.523      | 39.55                         | 73.91                  | 2.233      | 40.57                         |
| 72.98                            | 2.444      | 40.88                         | 76.03                  | 2.178      | 41.03                         |
| 75.38                            | 2.371      | 41.66                         | 78.19                  | 2.118      | 42.21                         |
| 77.72                            | 2.322      | 42.66                         | 80.29                  | 2.137      | 42.82                         |
| 79.99                            | 2.286      | 43.41                         | 82.34                  | 2.023      | 43.95                         |
| 82.02                            | 1.773      | 44.08                         |                        |            |                               |
| 84.07                            | 2.162      | 44.80                         |                        |            |                               |
| 86.23                            | 2.112      | 45.94                         |                        |            |                               |

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### Summary

The heat capacity of nickel nitrate hexammoniate has been determined from 54 to 300°K. The substance undergoes a gradual transition between 173 and 247°K., with the maximum heat capacity occurring at 243.3°K. The heat of transition is 1818 calories per mole, and the corresponding entropy is  $7.65 \pm 0.5$  E. U. The transition exhibits supercooling effects. There is an additional region of anomalous thermal behavior below 80°K.

The upper transition is discussed from the point of view of order and disorder in the orientation of nitrate groups in the crystal lattice.

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