BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1833—1844 (1967)

# Heat Capacities and Thermodynamic Properties of Ammonium Nitrate Crystal: Phase Transitions between Stable and Metastable Phases[†1]

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(Received March 22, 1967)

The heat capacities of ammonium nitrate were measured between 15 and 410°K for the stable and metastable phases by use of adiabatic- and conduction-type calorimeters. The phase transformations between stable phases; *i. e.*, V—IV, IV—III, III—II and II—I, and the metastable one between IV and II, were all found to be of first-order type. The direct transition between V and II, which is only realized for the sample treated with a minute amount of surface active agent, was ascertained to be typical higher-order type. Heat and entropy of transition of five kinds of transitions were determined. These results conclude that the heat capacity data by Stephenson *et al.* at low temperature region are much more reliable than the recent values by Eichenauer *et al.* The possibility of the existence of the seventh phase below 156°K has been proposed.

Since the discovery of anomalous peak in specific heat curve of ammonium chloride by Simon *et al.* in 1927, there have been accumulated so many results with calorimetric investigations on various kinds of ammonium salts. These informations together with a variety of physical properties obtained have been attracting many people to understand this effect more in detail from theoretical as well as experimental points of view.

On the other hand, mainly Finnish workers performed systematic calorimetric studies of various kinds of metal nitrate crystals which also exhibit similar kind of phase transitions due to the disordered orientation of nitrate ion. A review article on the relationship between the entropy of transition and crystal structure change on these compounds has been published quite recently by Newns and Staveley.1)

The present material, ammonium nitrate composed of these two, ammonium and nitrate ions, is

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[†1] Read before the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, 1966.

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1) D. M. Newns and L. A. K. Staveley, *Chem. Revs.*, **66**, 267 (1966).

TABLE 1. CRYSTAL STRUCTURES AND PHASE TRANSITIONS IN $NH_4NO_3$

| Transition point, °K | | | 256.2[5] | | 305.38[6] | | 357.25[7] | | 399.00[7] | |
|---|---|---|---|---|---|---|---|---|---|---|
| Crystal system<br>Space-group | ? | Tetragonal<br>$C_4^3$-$P4_2$ | | Orthorhombic<br>$V_h^{13}$-$Pmmn$ | | Orthorhombic<br>$V_h^{16}$-$Pbnm$ | | Tetragonal<br>$C_{4v}^2$-$P4bm$ | | Cubic<br>(CsCl-type) |
| Phase | (VII) | V | | IV | | III | | II | | I |
| Metastable transition | | | | | | 324°K | | | | |
| | | | 315°K | | V* | | 318°K | | | |

still a very interesting substance to study in these respects and indeed demonstrates many phase transitions of rather complex nature. Already in 1932, three papers were published independently, with regard to the crystal structure and thermal properties, by Hendricks, Posnjak and Kracek,[2] West,[3] and by Grenshaw and Ritter.[4] Since then, these studies interested many workers from the point of above-mentioned order-disorder orientational rearrangement of ammonium and nitrate ions in the lattice.

Through the effort of these investigations, this crystal is known to exist in at least five solid phases at ordinary pressures. These modifications with the pertinent data on crystal structure and transition points are given in Table 1.

A sixth phase is reported to be stable above 442°K at pressures higher than 9000 kg/cm$^2$ by Bridgman.[8] There remains, however, still seemingly somewhat contradicting or unsolved problems on a possibility of the existence of the seventh modification at lower temperature, suggested by spectroscopic, thermal or other studies by Crenshaw and Ritter,[4] Jaffrey,[9] Vol'fkovich *et al.*,[10] Theoret and Sandorfy[11] and others.

As to the specific heat itself, it has been believed that the precise measurement by Stephenson *et al.*[5] established the conclusive data below 315°K. Quite recently, however, Eichenauer and Liebscher[12] published a new result which is deviating considerably at higher temperature region from the data by Stephenson *et al.*

In the present study we have measured the specific heat from 15 to 410°K with focusing our special attention on the following few points: i) To reexamine the reliability of the recent data of specific heat by Stephenson *et al.* and Eichenauer *et al.*, ii) To check the possibility of presence of the seventh modification, iii) To establish the free energy relationship between all conditions governing the direct transformation from phase II to V which was first suggested by Amoros *et al.*[13] from structural view point and later really found by one of the present authors[14] by treating the sample with minute amount of surface active agent, and iv) To establish the reliable numerical data of enthalpies of each transitions.

The last point concerns with the differential thermal analysis method in which almost all workers check the availability of their instruments with the detection of the phase transitions of this compound, notwithstanding that there is no complete set of their reliable data.

## Experimental

**Materials.** A special, reagent-grade ammonium nitrate (Nakarai Chem. Ind. Ltd.) was recrystallized twice from ethyl alcohol (special-grade, Wakô Chem. Ind. Ltd.), and then dried under high vacuum ($10^{-6}$ mmHg) for 10 hr. This sample was then powdered. This drying and powdering procedures were repeated three times, one after the other, in order to remove completely the occluded mother liquor.

A specimen used for the measurement of the specific heat of metastable phase transition between phase V and II was prepared by adding a small amount of additive to the original specimen, and this is referred to as "specimen-add' hereafter.† The additive used for the present work is octadecylamine acetate, the amount of which is about 0.2 wt%. The additive was prepared by neutralization of octadecylamine (Wakô Chem. Ind. Ltd.) with acetic acid, according to the ordinary method. The procedure taken for

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2) S. B. Hendricks, E. Posnjak and P. C. Kracek, *J. Am. Chem. Soc.*, **54**, 2766 (1932).

3) C. W. West, *ibid.*, **54**, 2256 (1932).

4) J. L. Crenshaw and I. Ritter, *Z. physik. Chem.*, **B 16**, 143 (1932).

5) C. C. Stephenson, D. R. Bentz and D. A. Stevenson, *J. Am. Chem. Soc.*, **77**, 2161 (1955).

6) D. H. Everet and A. E. P. Watson, *Trabajos reunion intern. reactividad solidos*, 3°, Madrid, 1956, **1**, 301—319.

7) V. Hovi, J. Pöyhönen and P. Paalassalo, *Ann. Acad. Sci. Fennicae, Ser. A VI*, **42**, 3 (1960).

8) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **51**, 605 (1916).

9) J. Jaffrey, *Compt. rend.*, **224**, 1346 (1947).

10) S. I. Vol'fkovich, S. M. Rubinchik and V. M. Kpzhin, *Izvest. Akad. Nauk. S. S. S. R., Otdel. Khim. Nauk.*, **1954**, 209.

11) A. Theoret and C. Sandorfy, *Can. J. Chem.*, **42**, 57 (1964).

12) W. Eichenauer and D. Liebscher, *Z. Naturforsch.*, **20a**, 160 (1965).

13) J. L. Amoros Portoles and R. L. Banerjee, *Bol. R. Soc. Esp. Hist. Nat. (G)*, **58**, 165 (1965).

14) M. Nagatani, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 424 (1965); **68**, 1842 (1965).

† See Ref. 5 for the effect of some additives on the phase transitions.

TABLE 2. SELECTED VALUES FOR HEAT CAPACITY OF $NH_4NO_3$

| $T_{av}$ °K | $\Delta H/\Delta T$ J/(mol·deg K) | Approx. $\Delta T$ |
|---|---|---|
| | Series 1 | |
| 270.14 | 129.20 | 1.659 |
| 273.44 | 130.26 | 1.649 |
| 276.93 | 131.60 | 2.078 |
| 281.07 | 132.91 | 2.061 |
| 285.15 | 134.76 | 2.039 |
| 288.24 | 135.79 | 2.026 |
| 292.23 | 137.18 | 2.009 |
| 296.28 | 138.84 | 1.989 |
| 300.25 | 139.96 | 1.976 |
| 302.99 | 141.55 | 1.879 |
| 306.73 | 142.88 | 1.867 |
| | Series 2 | |
| 305.16 | 118.70 | 1.989 |
| 307.13 | 119.80 | 1.977 |
| 309.10 | 120.48 | 1.968 |
| 311.06 | 120.99 | 1.962 |
| 313.02 | 121.04 | 1.960 |
| 314.97 | 121.52 | 1.953 |
| 316.92 | 121.70 | 1.950 |
| 318.87 | 122.37 | 1.942 |
| 320.80 | 122.51 | 1.940 |
| 322.73 | 123.24 | 1.931 |
| 324.65 | 124.21 | 1.921 |
| | Series 3 | |
| 15.50 | 1.952 | 3.012 |
| 18.05 | 3.165 | 2.042 |
| 20.01 | 4.188 | 1.833 |
| 21.87 | 5.335 | 1.879 |
| 23.64 | 6.627 | 1.662 |
| 25.57 | 7.975 | 2.117 |
| 27.68 | 9.602 | 2.117 |
| 29.84 | 11.452 | 2.197 |
| 31.80 | 13.067 | 1.704 |
| 33.63 | 14.61 | 1.935 |
| 35.65 | 16.38 | 2.108 |
| 37.82 | 18.23 | 2.240 |
| 42.21 | 21.87 | 1.848 |
| 46.51 | 25.27 | 2.594 |
| 51.37 | 28.98 | 2.291 |
| 55.56 | 32.16 | 2.182 |
| 60.17 | 35.64 | 2.288 |
| 64.58 | 39.04 | 2.131 |
| 68.59 | 41.50 | 2.027 |
| 73.13 | 44.42 | 2.319 |
| 77.66 | 47.28 | 2.205 |
| 82.31 | 50.23 | 2.329 |
| 86.88 | 52.84 | 2.236 |
| 91.47 | 55.44 | 2.294 |
| 95.99 | 57.70 | 2.223 |
| 98.60 | 59.17 | 2.191 |
| 102.92 | 61.17 | 2.134 |
| 107.14 | 63.15 | 2.083 |
| 111.26 | 64.93 | 2.036 |
| 115.29 | 67.02 | 1.992 |
| 119.36 | 69.02 | 2.034 |
| 123.39 | 70.76 | 1.996 |
| 127.86 | 72.99 | 2.293 |
| 132.40 | 74.95 | 2.248 |
| 136.99 | 77.07 | 2.178 |
| 141.34 | 78.80 | 2.162 |
| 145.69 | 81.11 | 2.277 |
| 150.21 | 83.11 | 2.238 |
| 154.64 | 85.51 | 2.197 |
| 156.92 | 85.91 | 2.362 |
| 159.28 | 86.93 | 2.342 |
| 163.92 | 88.92 | 2.303 |
| 168.55 | 91.17 | 2.396 |
| 173.31 | 93.07 | 2.360 |
| 177.99 | 95.07 | 2.324 |
| 182.61 | 97.21 | 2.288 |
| 187.22 | 99.14 | 2.388 |
| 191.95 | 101.51 | 2.349 |
| 196.33 | 103.49 | 2.321 |
| 202.65 | 106.29 | 3.414 |
| 208.86 | 108.85 | 2.237 |
| 213.30 | 111.19 | 2.209 |
| 218.78 | 113.87 | 2.177 |
| 223.10 | 115.77 | 2.145 |
| 227.39 | 117.64 | 2.185 |
| 231.64 | 119.84 | 2.096 |
| 235.83 | 121.44 | 2.073 |
| 240.01 | 123.48 | 2.098 |
| 244.18 | 125.25 | 2.075 |
| 248.31 | 127.24 | 2.052 |
| 253.41 | 129.59 | 2.024 |
| | Series 4 | |
| 144.98 | 80.99 | 1.960 |
| 146.94 | 81.72 | 1.945 |
| 148.87 | 82.42 | 1.930 |
| 150.77 | 83.29 | 1.855 |
| 152.61 | 84.34 | 1.838 |
| 154.46 | 85.40 | 1.845 |
| 156.29 | 85.90 | 1.815 |
| 158.10 | 86.47 | 1.804 |
| 159.90 | 87.19 | 1.792 |
| | Series 5 | |
| 140.10 | 78.61 | 1.742 |
| 141.83 | 79.53 | 1.727 |
| 143.55 | 80.38 | 1.713 |
| 151.99 | 84.11 | 1.664 |
| 153.65 | 85.00 | 1.651 |
| 155.29 | 85.68 | 1.641 |
| 156.93 | 85.96 | 1.635 |
| 158.56 | 86.73 | 1.624 |
| 160.18 | 87.38 | 1.614 |

Table 2. (Continued)

| $T_{av}$ °K | $\Delta H/\Delta T$ J/(mol·deg K) | Approx. $\Delta T$ | $T_{av}$ °K | $\Delta H/\Delta T$ J/(mol·deg K) | Approx. $\Delta T$ |
|---|---|---|---|---|---|
| 195.26 | 102.90 | 1.665 | 259.04 | 124.59 | 1.989 |
| 196.92 | 103.41 | 1.659 | 263.50 | 126.33 | 2.113 |
| 198.57 | 104.07 | 1.651 | 267.70 | 128.01 | 2.081 |
| 200.22 | 104.89 | 1.641 | 269.48 | 128.34 | 2.086 |
| 201.86 | 105.61 | 1.633 | 273.63 | 130.15 | 2.061 |
| 252.78 | 128.53 | 1.954 | 277.76 | 131.73 | 2.066 |
| 254.73 | 129.55 | 1.943 | 282.03 | 133.01 | 2.149 |
| 256.67 | 130.19 | 1.935 | 286.31 | 134.33 | 2.129 |
| 258.60 | 131.34 | 1.923 | 290.55 | 135.59 | 2.112 |
|  |  |  | 294.73 | 137.24 | 2.090 |
|  | Series 6 |  | 298.91 | 138.65 | 2.072 |
| 255.05 | 123.39 | 2.006 | 303.04 | 139.81 | 2.056 |

addition was as follows: The additive was dissolved into benzene (special-grade, Wakô Chem. Ind. Ltd.), and pure ammonium nitrate was soaked into this solution. After vigorous stirring of the soaked specimen in the solution, the liquid benzene was evaporated completely at room temperature. For introducing the specimen into the calorimeter cell a vacuum-type dry box filled with dry nitrogen gas was employed for avoiding the humidity from the sample.

**Apparatus and Method.** The heat capacities of stable phases between 15 and 320°K were measured with an automatically controlled low-temperature adiabatic calorimeter, the details of which have been reported previously.[15] The weight of the sample used was 18.4883 g *in vacuo*, or 0.23069 mol at a molecular weight of 80.048.

The measurements between 275 and 410°K for pure specimen and that between 275 and 340°K for specimen-add were the same in its main features as the one used hitherto in this laboratory.[16]

Standard substances used for the calibration of the conduction-type calcorimeter were mainly benzoic acid and potassium chloride for the higher temperature region. This benzoic acid was obtained through the courtesy of E. J. Prosen of the Chemistry Division of the National Bureau of Standards as a Calorimetry Conference Standard specimen. The potassium chloride was obtained by recrystallization of the salt (Special-grade, Wako Chem. Ind. Ltd.) from distilled water.

For the heat capacity of potassium chloride, the following equation given by Ziegler and Messer[17] was adopted;

$$C_P = 12.10 + 3.97\times10^{-3}t \quad (\text{cal mol}^{-1}\text{ deg}^{-1}), \qquad (1)$$

where, $t$ is temperature in °C. The data derived from this equation are smoothly connected with those by Berg and Morrison[18] below 270°K which are believed to be most reliable. In the present work, reliability of Eq. (1) was confirmed between 275 and 389°K by using the benzoic acid as a reference of heat capacity.

The weight of samples employed for the conduction-type calorimeter was 5.1536 g or 0.06438 mol for pure specimen and 4.8130 g or 0.06013 mol for specimen-add, respectively. The heating or cooling rate was 0.2—0.3°C/min, except the transition regions. In the operated temperature region, the experimental error of the conduction calorimeter is believed to be less than ±0.5%.

## Experimental Results

**Heat Capacity.** The results obtained are presented in three parts as follows; (1) the data by the adiabatic calorimeter for pure specimen, (2) the data by the conduction-type calorimeter for pure specimen and (3) the data by the conduction-type calorimeter for specimen-add.

(1) The heat capacities observed by use of the adiabatic calorimeter are listed in Table 2 in

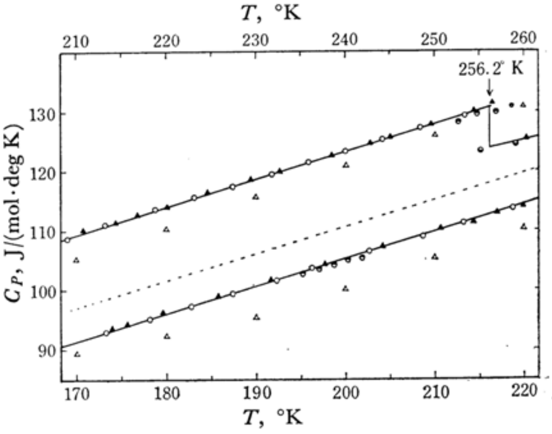

Fig. 1. The heat capacity of $NH_4NO_3$ between 170 and 260°K.

○ Series 3 ◓ Series 5 ◒ Series 6

▲ Stephenson *et al.*[5]

△ Eichenauer and Liebscher[12]

Temperature scale at the top is for the upper curves above the dotted line.

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[15] H. Suga and S. Seki, This Bulletin, **38**, 1000 (1965).

[16] S. Seki, M. Momotani, K. Nakatsu and T. Oshima, *ibid.*, **28**, 411 (1955).

[17] W. T. Ziegler and C. E. Messer, *J. Am. Chem. Soc.*, **63**, 2694 (1941).

[18] W. T. Berg and J. A. Morrison, *Proc. Roy. Soc. (London)*, **A242**, 467 (1957).

chronological order. They are the ratios of the increase in enthalpy, $\Delta H$, to the rise in temperature, $\Delta T$. Each value of $T_{av}$ in the table is the arithmetic mean of the initial and final temperatures of the corresponding $\Delta T$. The ice point is taken to be 273.15°K.

As is shown in Figs. 1 and 2 the heat capacities reported by Stephenson *et al.*[5] agree quite well with the present results in the whole temperature region with deviations less than 1%. In our measurement, however, it has been recognized that the observed heat capacities depend on the history of the sample (Figs. 1 and 3). This fact will be explained and discussed later.

While, the data given by Eichenauer and Liebscher[12] deviate much largely from ours, in particular at higher temperature region of phase V, and furthermore in phase IV.

We have found, however, that there is a very small anomaly at 156°K which is clearly recognized to be outside of our experimental error. This part was measured repeatedly three times and the results are shown graphically in Fig. 2 in exaggerated scale. As to this anomalous effect we should like to refer later again.

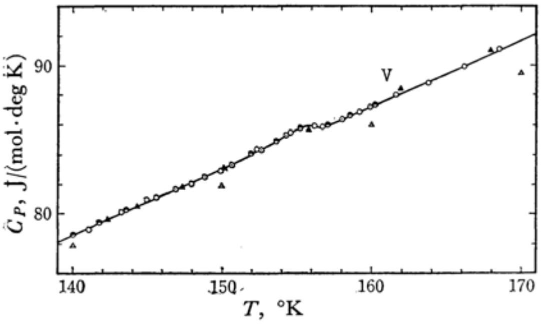

Fig. 2. The heat capacity of $NH_4NO_3$. (the small anomaly around 156°K).
○ Series 3 ⊙ Series 4 ◒ Series 5
▲ Stephenson *et al.*[5]
△ Eichenauer and Liebscher[12]

(2) The heat capacities measured for pure specimen with the conduction-type calorimeter are listed in Table 3. They are $\Delta H/\Delta T$ as mentioned above, their approximate temperature ranges, $\Delta T$, being shown in the last column.

These data are plotted in Fig. 3 with some results by the adiabatic calorimeter.

Phase II below 357.25°K is of metastable state and appeared only in the cooling measurement after heating the sample up to phase I. The heat capacities of phase II measured in cooling direction increase with decreasing temperature in the region below about 350°K.

Validity of this tendency was ascertained by getting the identical results with the repetition of measurement in cooling and heating directions between 325 and 350°K.

TABLE 3. SELECTED VALUES FOR HEAT CAPACITY OF $NH_4NO_3$

| $T_{av}$ °K | $\Delta H/\Delta T$ J/(mol·deg K) | Approx. $\Delta T$ |
|---|---|---|
| | (Phase IV) | |
| 275.69 | 131.8 | 2.53 |
| 280.75 | 133.5 | 2.53 |
| 285.77 | 135.0 | 2.52 |
| 290.75 | 137.5 | 2.52 |
| 295.69 | 138.5 | 2.47 |
| 300.60 | 140.2 | 2.45 |
| 305.46 | 142.2 | 2.43 |
| 310.29 | 143.2 | 2.41 |
| | (Phase III) | |
| 303.01 | 118.8 | 2.43 |
| 305.46 | 119.4 | 2.43 |
| 310.29 | 120.5 | 2.41 |
| 315.08 | 121.0 | 2.39 |
| 319.83 | 122.0 | 2.37 |
| 324.55 | 123.5 | 2.35 |
| 329.23 | 124.4 | 2.33 |
| 336.19 | 125.0 | 2.31 |
| 340.78 | 126.2 | 2.29 |
| 345.38 | 127.1 | 2.27 |
| 349.86 | 127.7 | 2.26 |
| 354.35 | 129.2 | 2.24 |
| 356.59 | 129.4 | 2.23 |
| | (Phase II) | |
| 322.20 | 157.5 | 2.35 |
| 324.55 | 153.9 | 2.35 |
| 326.89 | 151.9 | 2.34 |
| 329.23 | 151.7 | 2.34 |
| 331.56 | 151.0 | 2.32 |
| 333.88 | 149.5 | 2.32 |
| 336.19 | 149.0 | 2.31 |
| 340.78 | 148.7 | 2.29 |
| 345.34 | 148.4 | 2.27 |
| 349.86 | 147.9 | 2.26 |
| 354.35 | 147.3 | 2.24 |
| 361.03 | 147.5 | 2.22 |
| 365.43 | 147.3 | 2.21 |
| 369.81 | 147.5 | 2.19 |
| 376.31 | 148.5 | 2.16 |
| 380.61 | 149.0 | 2.14 |
| 384.88 | 149.8 | 2.13 |
| 391.21 | 150.6 | 2.11 |
| 395.40 | 152.4 | 2.09 |
| 398.01 | 152.5 | 2.08 |
| | (Phase I) | |
| 401.63 | 159.6 | 2.07 |
| 403.69 | 160.5 | 2.06 |
| 407.79 | 160.9 | 2.05 |
| 411.87 | 161.0 | 2.04 |

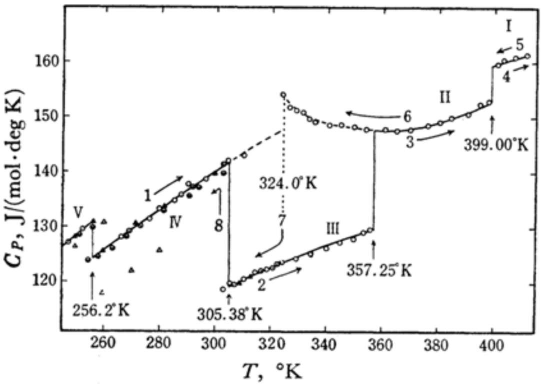

Fig. 3. The heat capacity of $NH_4NO_3$. (Phases IV, III, II and I)

○ From Table 3
◒ From series 5 or 6 in Table 2
⊙ From series 1, 2 or 3 in Table 2
▲ Stephenson *et al*[5)]
△ Eichenauer and Liebscher[12)]

Numbered arrows show the order and directions of one of experimental series with the conduction-type calorimeter.

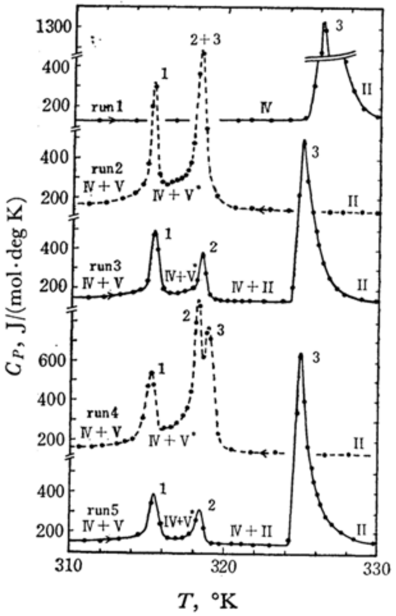

Fig. 4. Metastable phase transitions IV-II and V-V*-II appeared in $NH_4NO_3$-add.
Peak 1: V-V* Peak 2: V*-II
Peak 3: IV-II

(3) The measurements with specimen-add were repeated three times by heating and succesive cooling procedures in the temperature range from 275 to 340°K. All the features obtained by this process of measurement near the phase transition were reproduced in Fig. 4.

In the first heating (run 1) of the virgin specimen, transition IV→II occurs and in the successive run in cooling direction (run 2), transitions II→IV and II→V* take place at around 319°K and then the latter is followed by the V*→V transition*, so the starting material for the run 3 is the mixture of V and IV. In the run 5, the proportion of transition IV→II showed an increasing tendency compared to the run 3, but in these experiments, the phase III which is most stable in the region between 305 and 357°K did not appear at all. The polymorphic modification of the sample and the assignments of the observed peaks of heat capacities are also shown in Fig. 4.

The differential thermal analysis curves of transitions V-V*-II which are free from transition IV-II are depicted in Fig. 5 for reference. This heating curve is similar in its shape to the transitions V-V*-II of runs 3 and 5 in Fig. 4. With an assumption that the proportion of the V-V*-II part of the sample was kept constant during the heating process (runs 3 and 5), heat capacity of the each metastable phase was estimated by the following calculation;

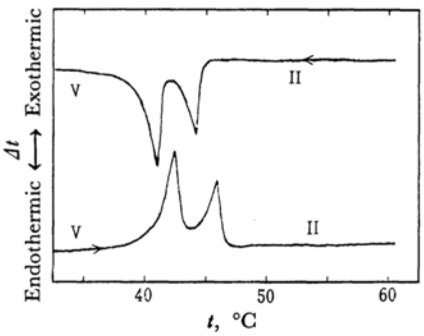

Fig. 5. Differential thermal analysis curves for transition V-V*-II in $NH_4NO_3$-add[14)].

$$C_P(\text{est.}) = 1/0.430[C_P(\text{run 3}) - C_P(\text{run 1})] + C_P(\text{run 1}) \tag{2}$$

Where $C_P$(est.) stands for the heat capacity of phase V, V* or II; $C_P$(run 1), $C_P$(run 3), the observed heat capacity in each run; and the value 0.430, the fraction which undergoes the transition V-V*-II in run 3. This value was determined by comparison of the apparent heats of transition IV-II in run 1 and 3, and equating it to [1-$\Delta H$(run 3)/$\Delta H$(run 1)], where $\Delta H$(run 1) and $\Delta H$(run 3) were 1860 and 1060 ($\Delta H$(run 5)=1270) J/mol, respectively.

The heat capacities determined by this procedure are listed in Table 4. The estimation with the data in run 5 instead of those in run 3 is also possible, but this procedure was abandoned, since the results are rather uncertain due to the smaller fraction of the transition V-V*-II part.

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† The appearence of the metastable V* phase cited here were originally confirmed by DTA and X-ray methods (see Ref. 14).

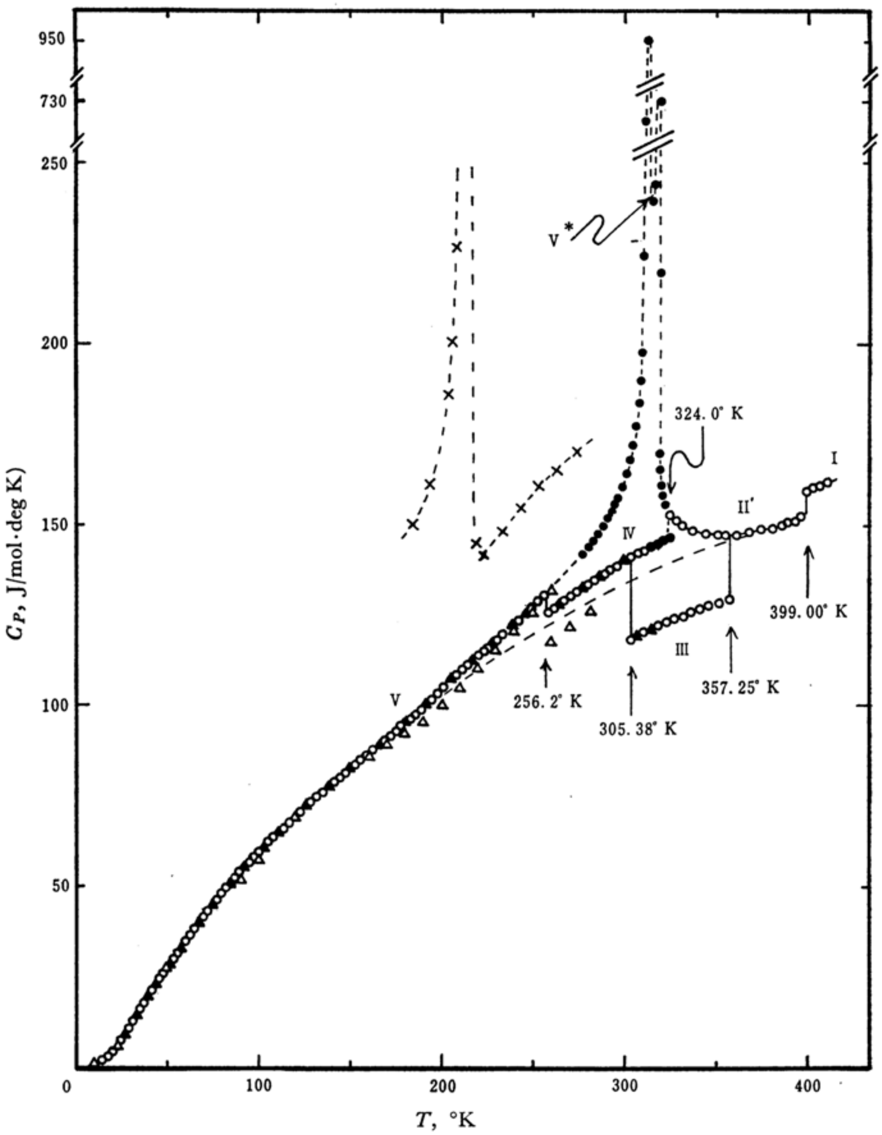

Fig. 6. The heat capacity of $NH_4NO_3$.

○ Pure $NH_4NO_3$
▲ Stephenson *et al*5)
× Crenshaw and Ritter4)
● $NH_4NO_3$-add
△ Eichenauer and Liebscher12)

All the heat capacities experimentally determined by the present work are presented graphically in Fig. 6, together with the results by Eichenauer and Liebscher,12) Crenshaw and Ritter4) and Stephenson *et al.*5) We can see in this figure that the estimated heat capacities for the V-V*-II process are smoothly fitted to the extrapolated curves from the data around 260°K of phase V and from the values of metastable phase II around 324°K (Table 3). Here, the heat capacity of phase V in the range between 256 and 275°K was calculated by using the following equation;

$$C_P(\mathrm{V}) = 131.04 + 0.460(T - 256.2) + 3.68\times10^{-3}(T - 256.2)^2 \qquad (3)$$

Such an apparent continuity between the pure sample and the specimen-add indicates that the minute amount of the surface active agent does not affect the specific heat values, at least, within the experimental error.

**Temperatures, Enthalpies and Entropies of Transition.** The observed temperatures, enthalpies and entropies of the phase transition are summarized in Table 5. Transitions V-IV

TABLE 4. SELECTED VALUES FOR HEAT CAPACITY OF $NH_4NO_3$-ADD

| $T_{av}$ °K | $\Delta H/\Delta T$ J/(mol·deg K) | Approx. $\Delta T$ |
|---|---|---|
| | (Run 1) | |
| 278.23 | 132.6 | 2.53 |
| 283.27 | 134.4 | 2.52 |
| 288.27 | 135.7 | 2.52 |
| 293.23 | 137.2 | 2.47 |
| 298.15 | 139.0 | 2.45 |
| 303.03 | 140.4 | 2.43 |
| 307.88 | 141.5 | 2.41 |
| 312.69 | 142.7 | 2.39 |
| 315.08 | 143.3 | 2.38 |
| 317.46 | 143.9 | 2.37 |
| 319.83 | 144.5 | 2.36 |
| 322.20 | 145.1 | 2.35 |
| | (V-V*-II) | |
| 278.23 | 143.0 | 2.53 |
| 280.75 | 144.1 | 2.53 |
| 283.27 | 145.5 | 2.52 |
| 285.77 | 148.0 | 2.52 |
| 288.27 | 149.3 | 2.52 |
| 290.75 | 151.7 | 2.51 |
| 293.23 | 153.9 | 2.47 |
| 295.69 | 156.7 | 2.47 |
| 298.15 | 159.5 | 2.45 |
| 300.60 | 162.9 | 2.44 |
| 303.03 | 166.8 | 2.43 |
| 305.46 | 171.9 | 2.43 |
| 307.88 | 178.9 | 2.41 |
| 308.48 | 181.9 | 1.21 |
| 309.69 | 185.2 | 1.20 |
| 310.89 | 195.2 | 1.20 |
| 312.09 | 207.3 | 1.20 |
| 313.17 | 226.5 | 0.96 |
| 313.88 | 266.3 | 0.48 |
| 314.36 | 277.8 | 0.48 |
| 314.84 | 372.8 | 0.48 |
| 315.20 | 952.3 | 0.24 |
| 315.44 | 779.6 | 0.24 |
| 315.79 | 287.9 | 0.48 |
| 316.27 | 241.1 | 0.48 |
| 316.75 | 247.2 | 0.48 |
| 317.22 | 276.4 | 0.48 |
| 317.57 | 287.1 | 0.24 |
| 317.81 | 314.8 | 0.24 |
| 318.05 | 401.1 | 0.24 |
| 318.29 | 729.9 | 0.24 |
| 318.52 | 473.9 | 0.24 |
| 318.76 | 220.2 | 0.24 |
| 319.12 | 173.1 | 0.47 |
| 319.60 | 168.3 | 0.48 |
| 320.07 | 159.1 | 0.47 |
| 320.54 | 161.7 | 0.47 |
| 321.01 | 158.8 | 0.47 |
| 321.96 | 156.5 | 0.47 |

TABLE 5. TEMPERATURES, ENTHALPIES AND ENTROPIES OF TRANSITIONS OF $NH_4NO_3$

| Transition | $H_t$ °K | $\Delta H_t$ J/mol | $\Delta S_t$ J/(mol·deg K) |
|---|---|---|---|
| V-IV | — | 473± 6 | 1.85±0.02 |
| IV-III | — | 1700±10 | 5.57±0.03 |
| III-II | 357.2±0.1 | 1350±15 | 3.78±0.04 |
| | at 324.0°K | 590±10 | 1.82±0.03 |
| II-I | 399.0±0.05 | 4435±30 | 11.12±0.08 |
| IV-II | 324.0±0.4 | 1860±20 | 5.74±0.06 |
| V-V* | 315.2±0.1 | (3254) | (10.92) |
| V*-II | 318.2±0.1 | | |

Values in parentheses are estimated by assuming a normal heat capacity ($C_P=3.98+0.6219T-6.3357\times10^{-4}T^2$ J/(mol·deg K)) between 160 and 380°K.

and IV-III were so sluggish that their transition temperatures were not so precisely determined, the accuracies of their observed heats of transition being decreased.

An upper limit for the transition temperature of IV→II was determined by the measurements for specimen-add, and a lower limit for II→IV was obtained with pure specimen, since the transition IV→II did not take place in pure specimen and in the case of specimen-add transition II-IV was almost forbidden around the true transition temperature. The transition temperatures of V-V* and V*-II were taken respectively as these temperatures where the heat capacities reached the maximum values. As is shown in Fig. 4, these transitions are considered to be of higher-order, since the shape of the heat capacity curve is of characteristic λ-type with the maximum temperatures which are the same values in heating and cooling directions with no hysteresis.

The values of $T_t$ for the stable transitions in Table 5 agreed with those in Table 1 within the experimental error. However, the formers are slightly less accurate, so, in case of need, the latters may be adopted for the transition temperatures of the stable transitions.

In addition, metastable phase II which appeared also in pure specimen in the cooling curve transformed to phase III just below the transition point of IV-II, and consequently the heat of transition II→III at 324°K was estimated as 590±10 J/mol. This is also listed in Table 5.

## Thermodynamic Properties of Ammonium Nitrate

The values of heat capacity, entropy, and also of the enthalpy and Gibbs energy function of ammonium nitrate crystal at selected temperatures were listed in Tables 6, 7 and 8.

Table 6 is for the stable phases, and the values

TABLE 6. THERMODYNAMIC PROPERTIES OF $NH_4NO_3$ (STABLE PHASE) (in J/(mol·deg K))

| $T$, °K | $C_P°$ | $S°$ | $(H°-H_0°)/T$ | $-(G°-H_0°)/T$ |
|---|---|---|---|---|
| 5 | (0.068) | (0.023) | (0.017) | (0.006) |
| 10 | (0.546) | (0.182) | (0.136) | (0.046) |
| 15 | 1.83 | 0.615 | 0.459 | 0.156 |
| 20 | 4.21 | 1.442 | 1.076 | 0.366 |
| 30 | 11.53 | 4.473 | 3.291 | 1.181 |
| 40 | 20.07 | 8.970 | 6.427 | 2.542 |
| 50 | 27.95 | 14.312 | 9.960 | 4.352 |
| 60 | 35.61 | 20.102 | 13.612 | 6.490 |
| 70 | 42.38 | 26.113 | 17.250 | 8.862 |
| 80 | 48.74 | 32.206 | 20.807 | 11.399 |
| 90 | 54.60 | 38.296 | 24.246 | 14.050 |
| 100 | 59.87 | 44.321 | 27.544 | 16.776 |
| 120 | 68.78 | 56.067 | 33.715 | 22.352 |
| 140 | 78.45 | 67.436 | 39.451 | 27.984 |
| 160 | 87.28 | 78.515 | 44.904 | 33.611 |
| 180 | 96.06 | 89.299 | 50.097 | 39.202 |
| 200 | 105.02 | 99.881 | 55.139 | 44.742 |
| 220 | 114.18 | 110.32 | 60.085 | 50.230 |
| 240 | 123.47 | 120.65 | 64.984 | 55.668 |
| 256.2 | 131.04 | 128.97 | 68.924 | |
| 256.2±0.4[5] | Transition V–IV | | | 60.041 |
| 256.2 | 123.47 | 130.81 | 70.771 | |
| 260 | 125.10 | 132.64 | 71.553 | 61.038 |
| 280 | 132.84 | 142.20 | 75.658 | 66.541 |
| 298.15 | 139.08 | 150.81 | 79.362 | 71.447 |
| 300 | 139.65 | 151.60 | 79.702 | 71.900 |
| 305.38 | 141.27 | 154.10 | 80.772 | |
| 305.38±0.04[6] | Transition IV–III | | | 73.326 |
| 305.38 | 119.36 | 159.67 | 86.339 | |
| 320 | 122.22 | 165.31 | 87.913 | 77.400 |
| 340 | 126.1 | 172.84 | 90.046 | 82.794 |
| 357.25 | 129.5 | 179.17 | 91.871 | |
| 357.25±0.1[7] | Transition III–II | | | 87.295 |
| 357.25 | 147.3 | 182.94 | 95.649 | |
| 360 | 147.3 | 184.07 | 96.044 | 88.030 |
| 380 | 148.8 | 192.06 | 98.767 | 93.297 |
| 399 | 153.4 | 199.42 | 101.25 | |
| 399.00±0.01[7] | Transition II–I | | | 98.175 |
| 399 | 159.5 | 210.54 | 112.36 | |
| 400 | 159.7 | 210.94 | 112.48 | 98.457 |
| 410 | 161.0 | 214.90 | 113.65 | 101.25 |

of $C_P°$ at round values of temperature were determined by drawing the smoothed curves through the measured heat capacity data. In this procedure, however, the data in Series 5 and 6 of Table 2 were omitted for the reason mentioned later. The extrapolation below 15 to 0°K was made by Eq. (4)

$$C_P = 5.464\ T^3 \ \text{(in J/(mol·deg K); } T \text{ in °K)} \tag{4}$$

The error of the smoothed heat capacity data is estimated to be ±1% below 60°K, ±0.3% between 60 and 320°K, and ±0.5% above 320°K. The other thermodynamic quantities in the tables were derived from the smoothed heat capacity curves and the heat of transition data of the stable transitions in Table 5.

Table 7 is for the metastable states of phase IV and II in the temperature range where phase III is most stable. The thermodynamic properties of phases IV and II in this table were determined by continuous connection with the stable regions, respectively.

TABLE 7. THERMODYNAMIC PROPERTIES OF $NH_4NO_3$ (METASTABLE PHASES, IV AND II) (in J/(mol·deg K))

| $T$, °K | $C_P°$ | $S°$ | $(H°-H_0°)/T$ | $-(G°-H_0°)/T$ |
|---|---|---|---|---|
| 305 | 141.2 | 153.92 | 80.697 | 73.225 |
| 310 | 142.6 | 156.23 | 81.686 | 74.542 |
| 315 | 144.0 | 158.52 | 82.663 | 75.860 |
| 320 | 145.4 | 160.80 | 83.632 | 77.169 |
| 324 | 146.5 | 162.61 | 84.401 | 78.213 |
| 324.0±0.4 | Transition IV–II | | | |
| 324 | 154.8 | 168.34 | 90.127 | 78.212 |
| 326 | 153.2 | 169.29 | 90.519 | 78.767 |
| 328 | 151.9 | 170.22 | 90.897 | 79.321 |
| 330 | 151.2 | 171.14 | 91.264 | 79.875 |
| 332 | 150.7 | 172.05 | 91.624 | 80.428 |
| 335 | 150.0 | 173.40 | 92.149 | 81.254 |
| 340 | 149.1 | 175.62 | 92.994 | 82.626 |
| 345 | 148.3 | 177.79 | 93.800 | 83.989 |
| 350 | 147.8 | 179.92 | 94.575 | 85.345 |
| 355 | 147.4 | 182.02 | 95.324 | 86.692 |

Table 8 is for the metastable phases V, V* and II.

In this case, the values of entropy, enthalpy and Gibbs energy functions were calculated by numerical integrations with Eq. (2) and the estimated heat capacity data.

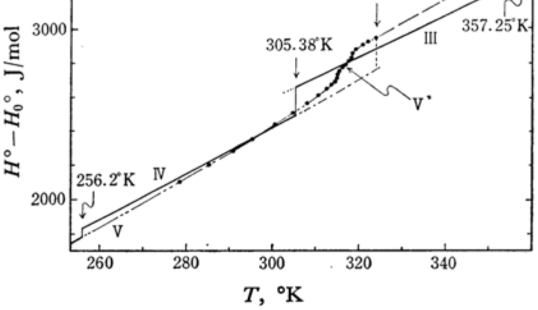

Fig. 7. Enthalpy *vs.* temperature curves of $NH_4NO_3$.
—·—·— Metastable phase V, V* or II in $NH_4NO_3$-add.

TABLE 8. THERMODYNAMIC PROPERTIES OF $NH_4NO_3$-ADD
(METASTABLE PHASES, V, V* AND II)
(in J/(mol·deg K))

| $T$, °K | $C_P$° | $S$° | $(H°-H_0°)/T$ | $-(G°-H_0°)/T$ |
|---|---|---|---|---|
| 256.2 | (131.0) | (128.96) | (68.924) | (60.041) |
| 260 | (132.8) | (130.91) | (69.845) | (61.062) |
| 265 | (135.4) | (133.46) | (71.058) | (62.404) |
| 270 | (138.1) | (136.02) | (72.273) | (63.744) |
| 278.23 | 143.0 | 140.23 | 74.291 | 65.943 |
| 285.77 | 148.0 | 144.11 | 76.158 | 67.955 |
| 290.75 | 151.7 | 146.67 | 77.415 | 69.255 |
| 295.69 | 156.7 | 149.29 | 78.695 | 70.597 |
| 300.60 | 162.9 | 151.92 | 80.016 | 71.902 |
| 305.46 | 171.9 | 154.60 | 81.403 | 73.198 |
| 309.08 | 184.0 | 156.70 | 82.531 | 74.164 |
| 311.49 | 201.0 | 158.17 | 83.362 | 74.806 |
| 313.64 | 242 | 159.66 | 84.272 | 75.385 |
| 314.12 | 270 | 160.06 | 84.550 | 75.513 |
| 314.60 | 315 | 160.49 | 84.843 | 75.642 |
| 315.08 | 660 | 161.05 | 85.280 | 75.772 |
| 315.2±0.1 Transition V-V* | | | | |
| 315.32 | ~950 | 161.77 | 85.934 | 75.836 |
| 315.55 | 610 | 162.36 | 86.458 | 75.901 |
| 316.03 | 243 | 162.79 | 86.761 | 76.032 |
| 316.51 | 242 | 163.16 | 86.994 | 76.163 |
| 316.98 | 256 | 163.53 | 87.234 | 76.294 |
| 317.46 | 277 | 163.94 | 87.518 | 76.425 |
| 317.70 | 304 | 164.16 | 87.667 | 76.490 |
| 317.93 | 340 | 164.39 | 87.837 | 76.555 |
| 318.77 | ~730 | 164.69 | 88.073 | 76.619 |
| 318.2±0.1 Transition V*-II | | | | |
| 318.41 | 620 | 165.24 | 88.548 | 76.687 |
| 318.65 | 264 | 165.59 | 88.836 | 76.753 |
| 318.88 | 179.5 | 165.75 | 88.933 | 76.820 |
| 319.36 | 170.5 | 166.01 | 89.058 | 76.952 |
| 320.78 | 160.5 | 166.73 | 89.387 | 77.346 |
| 321.62 | 157.3 | 167.20 | 89.615 | 77.582 |
| 324 | 154.8 | 168.35 | 90.107 | 78.244 |

The relationships in thermodynamic properties between the stable and metastable transition regions are presented graphically in Figs. 7 and 8, respectively.

In Fig. 8, however, the entropy and the enthalpy of phase V at 256.2°K are both taken to be zero as a standard point in order to show details of the mutual relations among the Gibbs energies.

The Gibbs energy curves of phases IV and II derived from Table 7 cross at 324.13°K which is compatible with the observed transition point of IV-II. Furthermore, the heats of transition for IV-II and III-II at 324.13°K are 1856 and 582 J/mol from Fig. 7, which are also consistent with the observed ones.

At 324°K, the values of entropy, enthalpy and Gibbs energy function of phase II in Table 7 are larger than those in Table 8 by −0.012, 0.02 and 0.032 in J/(mol·degK), respectively. Owing to the discrepancy of the two Gibbs energies, the cross point of the Gibbs energy curves of phase II (derived from Table 8) and phase IV (given in Table 7) appears somewhat lower than the observed limit of the transition point of the complete consistency. Considering the wide temperature range of the measurement for the metastable V-V*-II process, however, the inconsistency appeared on the transition point of IV-II is unavoidable due to the experimental error of heat capacity measurement, and the assumption used for the heat capacity estimation.

## Discussion

**(1) Specific Heat Values in Normal Regions.** *a) Phase V.* In Series 3 and 5 of Table 2, the experimental heat capacities of phase V at the higher temperatures show slight systematic disagreements between the two series. In Series 3, the sample was cooled down to 15°K prior to the measurement, while in Series 5, the sample was cooled down to 130°K. Stephenson *et al.*[5] have reported also a similar effect in the determination of the heat of transition V-IV. They found it was necessary to cool the sample below 120°K in order to get the correct values, the pre-cooling to 224°K giving the lower values by several percents. They considered that cooling to 224°K was insufficient to accomplish a complete conversion of phase IV to phase V.

*b) Phase IV.* Comparing the data of phase IV in Series 1 and 6 of Table 2 with each other, the similar situation found in phase V will also hold for the discrepancy between them, *i. e.*, the sample measured in Series 1 was a virgin sample of phase IV, whereas the sample measured in Series 6 seems to contain a small amount of phase III, the heat capacities of which are much lower than those of phase IV.

The measurements of the heat capacity of phase III were carried out in three series of different thermal history, and the results were in accordance with each other, showing no evidence of the incomplete conversion of phase IV to phase III.

As a cause for the persistence of phase III below the transition point of IV-III, it is reported by Whetstone[19] that such an impurity as potassium nitrate is effective for a dry sample.

If a dissolution-recrystallization mechanism[20] of transition IV-III causes inhomogeneity due to the segregation of the potassium impurity in the sample, it will be probable that a small impure part in the sample retains phase III even below 305.38°K.

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[19] J. Whetstone, *Acta Cryst.*, **7**, 697 (1954).

[20] R. N. Brown and A. C. McLaren, *Proc. Roy. Soc. (London)*, **A266**, 329 (1962).

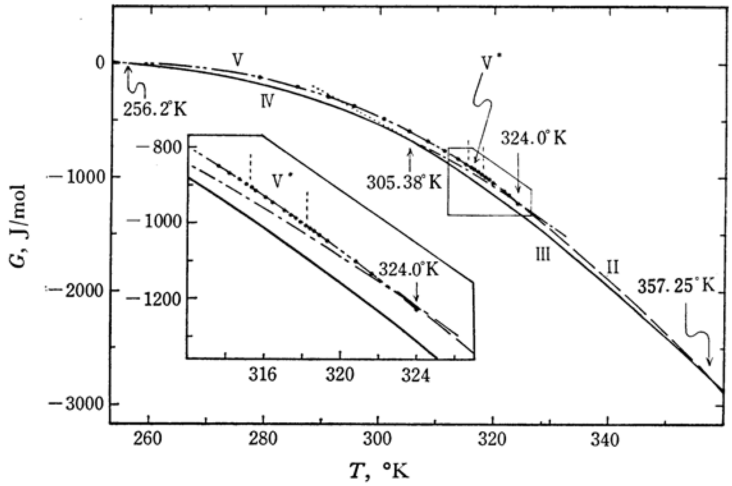

Fig. 8. Gibbs energy *vs.* temperature curves of $NH_4NO_3$. In this figure, the Gibbs energies are standardized at the state of phase V at 256.2°K, as follows;

$$G = H^\circ - H^\circ_{256.2}(\mathrm{V}) - T(S^\circ - S^\circ_{256.2}(\mathrm{V}))$$

---- Metastable phase V, V* or II in $NH_4NO_3$-add.

As there is no description about the sample they used, we cannot understand the reason why the heat capacity data obtained by Eichenauer and Liebscher[12] are significantly lower than Stephenson's and our data for phases IV and V in its higher temperature region. But, it may be one of the possibilities that their sample (V) contains some amount of remained phase III or IV.

**(2) Possibility of the Existence of Phase VII.** As is already described there is a number of papers which prove the existence of the seventh phase. But the evidences are not always so definite and some of them are contradicting with each other. The transition point at about −60°C reported by Crenshaw and Ritter,[4] and by Jaffrey[9] was not detected by the specific heat measurements by Stephenson *et al.,* Eichenauer *et al.* and by us. The only seemingly supporting result is the infrared study by Theoret and Sandorfy.[11] They suggest, however, that this transition point is not corresponding to the transition between IV and VII. Vol'fkovich *et al.,*[10] who first substantiated existence of phase VII, observed this phase at about −170°C, but they did not report the transition point between V and VII. Judging from these findings the true transition point between V and VII will lie between −60°C and −170°C. This expectation seems to be compatible with the observation by Newman and Halford.[21] They concluded the significant change in the infrared spectra must occur at temperature intermediate between −65 and −160°C. Taking these consistent observations into account, the small hump in specific heat curve at around 156°K (−117°C) found by us may be looked upon as a corresponding one. The slightness in its effect may be consisting with the facts that there is no noticeable change in the second moment of broad line NMR spectra by Goodwin and Whetstone,[22] Gutowsky *et al.*[23] and by Richards *et al.*[24] The only inconsistent report against this view is the transition point at around −160°C by Jaffrey.[9] But there is no description about the specific heat data, so we can not check the reliability of his measurement. Anyhow, it seems much desirable to check this transition point by using some other techniques.

**(3) Nature of Phase Transition between V, V* and II.** The transition between V and II, which really consists of two steps, shows somewhat different behaviors from the others. As is shown in Figs. 4 and 5, the specific heat curve shows a conspicuous maximum and the Gibbs energy curve shows no intersection with each other. These facts indicate that this phase transition is of higher order nature. Amoros *et al.*[25] have carried out the complete crystal structure analysis of phase V at lower temperature which is given in Fig. 9. According to their result, the molecular packing quite resembles that of phase II[13,26] which is shown in Fig. 10. They suggested that the phase II is a kind of vibra-

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[21] R. Newman and R. S. Halford, *J. Chem. Phys.,* **18**, 1291 (1950).

[22] T. H. Goodwin and J. Whetstone, *J. Chem. Soc.,* **1947**, 1455.

[23] H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.* **16**, 1164 (1948).

[24] R. E. Richards and T. Schaefer, *Trans. Faraday Soc.,* **57**, 210 (1961).

[25] J. L. Amoros Portoles, F. Arrese and M. L. Canut, *Z. Krist.,* **117**, 91 (1962).

[26] Y. Shinnaka, *J. Phys. Soc. Japan,* **11**, 393 (1956).

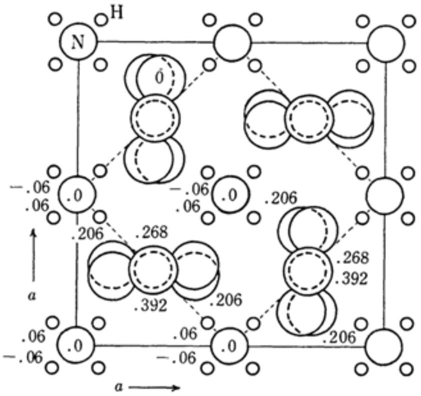

Fig. 9. A projection on the (001) plane of the crystal structure of phase V of $NH_4NO_3$.[25] $P4_2(C_4^3)$; $Z=8$; $a=7.98$, $c=9.78$ Å at −150°C

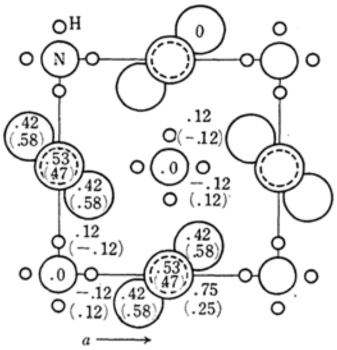

Fig. 10. A projection on the (001) plane of the crystal structure of phase II of $NH_4NO_3$.[13,26] $P4bm(C_{4v}^2)$; $Z=2$; $a=5.74$, $c=4.95$ Å

tional modification of phase V and will undergo the direct transformation from phase V under high pressure. One of the present authors, however, realized this transformation at ordinary pressure through the intermediate phase V* by utilizing the effect of surface active agent.[14] We should like to point out the features of this phase transition. As is shown in Fig. 4 and Fig. 6 this transition takes place very gradually over a wide range of temperature with no latent heat. Although the direct transition between phases V and II needs no displacement of the each center of gravity of ammonium and nitrate ions, this takes place by two steps *via* phase V*. X-Ray diffraction pattern obtained for the powder sample of phase V* is very similar to that of phase V as well as to phase II.[14] There may be pointed out some small differences as follows; in the pattern of phase V*, some reflections which correspond to (012), (124), (034) and (142) lines of phase V vanish, and in the pattern of phase II, furthermore (122), (014) and (032) lines assigned in regard to phase V disappear. According to the structure of phase V,[25] these reflections are attributed only to the hydrogen atoms. Although there is no detailed information about the state of nitrate ions in phase V*, the X-ray pattern of phase V* will assure that the lattice constants[†] and the positions of nitrogens are different only slightly among phases II, V* and V. Considering the total amount of entropy of transition, $\Delta S \approx 11$ (J/mol·degK) $\approx \boldsymbol{R}$ ln 4, this transition V-II may be a result of a kind of combined phenomenon of orientational order-disorder of both ammonium and nitrate groups.

## Summary

The heat capacities of ammonium nitrate were determined experimentally between 15 and 410°K for the stable and the metastable phases. There are four stable transitions of first-order in this interval, V-IV, IV-III, III-II, and II-I. Metastable transition IV-II of first-order type at 324.0°K and metastable one V-II were also realized. Transition V-II occurs in two steps *via* metastable phase V*. The transition points are found to be 315.2°K for V-V* and 318.2°K for V*-II, and these transitions are of higher-order type. The heat capacity of phase V* is 276 J/(mol·degK) at 317.2°K.

The heats of transition are found to be 473, 1700, 1350, 4435 and 1860 J/mol for transitions V-IV, IV-III, III-II, II-I and IV-II, respectively. The heat of transition and the entropy change were estimated for transition V-II as 3254 J/mol, and 10.92 J/(mol·degK), using an assumed normal heat capacity. Transition V-II is considered to occur as a combined phenomenon of orientational order-disorder of two ions, ammonium and nitrate groups. The thermodynamic functions have also been derived from the heat capacity data. The values at 298.15°K are, in units of J/(mol·degK): $C_P{}^\circ=139.1$, $S^\circ=150.81$, $(H^\circ-H_0{}^\circ)/\mathrm{T}=79.36$ and $-(G^\circ-H_0{}^\circ)/T=71.45$.

The authors wish to express their sincere thanks to Mr. A. Kimoto and Mr. N. Onodera for their assistances in the experimental work.

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[†] In Fig. 9, the pseudo unit cell ($a' \rightarrow a/\sqrt{2}$, $c' \rightarrow 2/c$) is illustrated by dotted line.