[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Heat Capacity of Ammonium Nitrate from 15 to 315°K.

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The heat capacity of ammonium nitrate has been measured between 15 and 315°K. There are two first-order transitions in this interval. The heat of transition (V → IV) is 110.8 cal. mole^{-1} at 256.2°K.; the heat of transition (IV → III) is 409.9 cal. mole^{-1} at 305.4°K. There was no evidence of the gradual transition reported by Crenshaw and Ritter. The entropy of ammonium nitrate (phase IV) at 298.16°K. was calculated as 36.11 ± 0.05 cal. deg.$^{-1}$ mole^{-1}. The standard free energy of formation of crystalline ammonium nitrate and the standard entropy of the ammonium ion (26.6 ± 0.4 cal. deg.$^{-1}$ mole^{-1}) were calculated from the value above and other thermodynamic data. An analysis of the heat capacity below 100°K. yielded estimates for the frequencies of torsional oscillation of the nitrate ion and the ammonium ion in phase V. The heat capacity of phase IV at 305.4°K. is 5.3 cal. deg.$^{-1}$ mole^{-1} greater than the heat capacity of phase III at this temperature. The decrease in heat capacity with increasing temperature is attributed to rotation of the ammonium ion in phase III, in contrast to fully excited torsional oscillation in phase IV.

The appearance of anomalies in the heat capacities of a number of ammonium salts was originally attributed to the onset of rotation of the ammonium ion.[2] However, the gradual transitions in ammonium chloride, bromide and iodide have been successfully interpreted as order–disorder transitions by means of heat capacity studies,[3] neutron-diffraction experiments,[4] and spectroscopic measurements.[5] In some other cases, the anomaly found in the heat capacity of the ammonium salt is also found in the corresponding potassium salt and cannot be attributed to the ammonium ion. A gradual transition has been reported in ammonium nitrate by Crenshaw and Ritter[6] at 213°K., although several other investigators failed to confirm the existence of any irregularity of the heat capacity in this region. Ammonium nitrate is known to exist in at least five solid phases at ordinary pressures, and a study of its heat capacity provides an unusual opportunity for examining the behavior of the ammonium ion in different crystalline environments.

Various physical properties of the five distinct crystalline phases of ammonium nitrate have been reported by many authors.[7] These modifications, with the reported limits of stability are: I, 442.8 to 398°K.; II, 398 to 356°K.; III, 356 to 305.4°K.; IV, 305.4 to 256.2°K.; and V, below 256.2°K. A sixth phase is reported stable at elevated temperature and pressures by Bridgman.[8]

In this investigation, measurements of the heat capacity have been made throughout the region in which modification V and IV are stable, *i.e.*, from 15 to 305.4°K., and in the region of stability for modification III to 315°K. These results have been represented by Debye and Einstein functions below 100°K., yielding estimates of the frequencies of torsional oscillation of the nitrate and ammonium ions in phase V. The heats of transformation and transition temperatures for the changes V to IV and IV to III have been determined. The entropy of ammonium nitrate (phase IV) at 298.16°K. was calculated, and the standard free energy of formation of ammonium nitrate and the standard entropy of the ammonium ion were calculated from the entropy of the solid and other thermodynamic data.

The fact that the heat capacity of phase III is lower than that of phase IV is attributed to rotation of the ammonium ion in phase III, in contrast to fully excited torsional oscillation in phase IV.

Materials.—All measurements were made on Merck reagent-grade ammonium nitrate. Analyses of this material gave an ammonia content of 21.28% by weight using a modified Kjeldahl method. The calculated percentage of ammonia in ammonium nitrate is 21.28. The sample was dried for 48 hours at 110°. The absence of abnormal values for the heat capacities in the region of the ice point, and the sluggish behavior of the material in phase transformations, confirm the absence of water.

The weight, *in vacuo*, of sample used was 119.654 g., or 1.495 moles at a molecular weight of 80.048.

Apparatus and Method.—The calorimeter and cryostat have been described previously.[9] The calorie was taken to be 4.1833 international joules, and the absolute temperature of the ice point was taken as 273.16°K.

Heat Capacity Measurements.—The experimental heat capacities from 15 to 315°K. are listed in Table I and presented graphically in Fig. 1. There are no irregularities in the molar heat capacity, excepting the discontinuities at

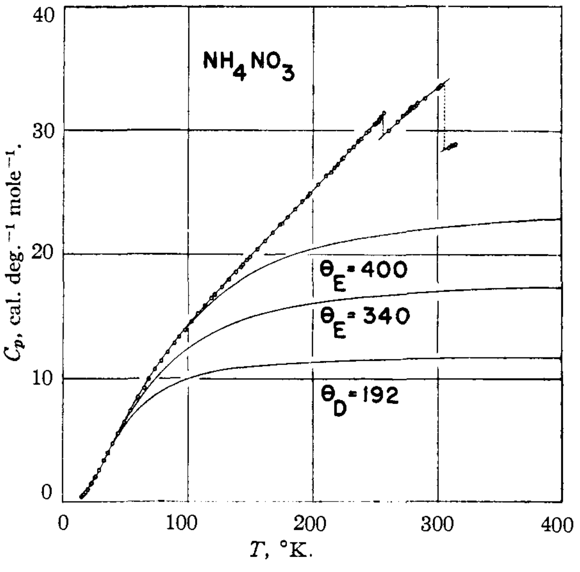

Fig. 1.—The heat capacity of NH_4NO_3.

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[1] Union Carbide and Carbon Fellow, academic year 1952–1953.

[2] L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

[3] C. C. Stephenson, R. W. Blue and J. W. Stout, *J. Chem. Phys.*, **20**, 1046 (1952).

[4] H. A. Levy and S. W. Peterson, *Phys. Rev.*, **86**, 766 (1952).

[5] E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 305 (1950).

[6] J. L. Crenshaw and I. Ritter, *Z. physik. Chem.*, **B16**, 143 (1932).

[7] Gmelin, "Handbuch der anorganischen Chemie," Verlag Chemie, Berlin, 1936, 8 Aufl., System-Nummer 23: Ammonium, Lieferung 1.

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

[9] R. W. Blue and J. F. G. Hicks, THIS JOURNAL, **59**, 1962 (1937).

the known first-order phase transformations. The values of the heat capacities reported by Crenshaw and Ritter[6] are so different from those reported here as to raise doubt that their sample was, in fact, ammonium nitrate. There is a possibility that their measurements were carried out on a metastable phase of ammonium nitrate; however, we were unable to supercool any of the high temperature phases of pure ammonium nitrate to the temperatures used by Crenshaw and Ritter. Numerous experiments were performed in a cooling-curve apparatus designed for rapid cooling on moist and dry, pure and impure, samples of ammonium nitrate in an effort to find the transition reported by Crenshaw and Ritter. There was no evidence of a transition at 212°K., nor was there any evidence of the transitions reported by Jaffrey,[10] one between 113 and 123°K., and the other between 208 and 216°K.

The values reported here are believed to be accurate to 0.2% above 35°K., to 1% at 20°K., and to 5% at 15°K.

TABLE I

THE HEAT CAPACITY OF AMMONIUM NITRATE (CAL./DEG./MOLE)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
15.12	0.43	78.82	11.46	179.56	23.00	252.78	30.91
16.01	.51	83.95	12.24	185.60	23.68	254.30	31.13
16.96	.60	89.10	12.91	191.61	24.29	256.80	31.46
18.25	.77	93.02	13.41	195.97	24.69	260.27	30.03
20.00	1.02	97.48	13.99	197.68	24.95	267.70	30.76
22.38	1.38	102.79	14.65	204.03	25.65	271.41	31.21
22.90	1.48	108.44	15.28	210.41	26.34	274.91	31.40
23.13	1.51	113.24	15.88	214.53	26.65	277.26	31.61
25.92	2.03	118.65	16.50	216.70	27.00	277.92	31.77
26.15	2.04	121.20	16.78	219.98	27.29	278.92	31.88
28.92	2.59	127.00	17.42	222.92	27.69	279.46	31.80
29.63	2.71	132.78	18.01	224.46	27.80	280.35	31.87
33.08	3.39	138.56	18.62	229.37	28.40	282.18	32.02
36.25	3.99	142.43	19.02	232.51	28.69	283.30	32.21
39.93	4.76	144.32	19.23	236.03	29.15	289.53	32.58
44.13	5.58	147.43	19.57	238.61	29.35	299.84	33.39
48.79	6.48	150.07	19.84	242.69	29.83	300.85	33.47
53.86	7.43	155.82	20.47	244.84	30.03	302.83	33.65
59.67	8.45	161.84	21.12	249.21	30.56	308.90	28.63
64.22	9.24	167.88	21.76	250.69	30.62	311.24	28.78
68.87	10.00	173.70	22.39	250.90	30.73	313.52	28.85
73.62	10.74	175.58	22.55	252.31	30.71	314.06	28.87

The Transition at 256.2°K.—The transition at 256.2°K. is a first-order conversion of phase V to IV, involving a change in crystal structure. The rate of this transformation was so slow that it was impossible to obtain an accurate value for the transition temperature using the dry sample in the calorimeter. The lowest temperature attained after 17 hours, during which adiabatic conditions were maintained, was about 260°K. when phase V was partially converted into phase IV. In the reverse procedure, when phase IV was partially converted into phase V, the highest temperature was only 250°K., leaving a region of indifference of 10°. The region of indifference was decreased by using a moist sample of ammonium nitrate in a cooling-curve apparatus. On cooling, the transition temperature of the wet sample was found to be 255.8°K., and on warming the transition occurred at 256.6°K. An average value, 256.2°K., has been taken as the transition temperature in the calculation of the heat of transition and in the determination of the entropy.

The sluggishness of this transformation decreased the accuracy of the determinations of the heat of transition. In order to ensure complete transformation of V to IV, it was necessary to heat the sample 20° above the transition temperature. The calculation of the heat of transition, which is comparatively small, required a large correction for $\int C_p dT$. The heat capacities could be measured quite accurately, of course, even on the supercooled and superheated phases. The results of five determinations of the heat of transition are listed in Table II, with the temperature to which the sample was cooled prior to the determination.

TABLE II

HEAT OF TRANSITION OF AMMONIUM NITRATE AT 256.2°K.

No.	ΔH (cal./mole)	Minimum cooling temp., °K.
1	105.2	224
2	96.3	224
3	110.1	121
4	110.2	64
5	112.2	32
Av. of 3, 4 and 5	110.8	

The first two determinations are significantly lower than the following three, a deviation which is undoubtedly due to incomplete conversion of modification IV to modification V on cooling. Cooling to 224°K. was insufficient to effect complete conversion to the low temperature phase, leading to low values for the heat of transformation when the sample was later warmed. This difficulty was anticipated because of the similar behavior of one of the transitions in ammonium iodide, and throughout the measurements a careful thermal history of the sample was recorded.

The last three values lie within the accuracy of the experimental determinations, when the large correction for $\int C_p dT$ is considered, and the average value, 110.8 cal./mole, has been used in the evaluation of the entropy.

The Transition at 305.4°K.—The transition in ammonium nitrate at 305.4°K. is a first-order conversion of NH_4NO_3(IV)-rhombic to NH_4NO_3(III)-rhombic, the latter being stable at temperatures above the transition temperature. Little of the experimental difficulty associated with the slow attainment of equilibrium observed at the transition at 256.2°K. was found in the transition at higher temperatures. A small amount of supercooling and superheating, giving a region of indifference of 0.2°K., prevented a determination of the transition temperature within the limits of accuracy of the thermometer. A minimum temperature of 305.53°K. was measured when the sample was brought into the transition by warming; on cooling, the measured temperature was 305.27°K. The transition temperature used in the entropy calculations is the average of those found on cooling and warming, 305.4°K.

The heat associated with the transition was measured twice, with complete conversion and with equilibrium conditions being established after relatively short time intervals in both cases. All heat capacities taken immediately following the determinations of the heat of transformation were normal.

These two determinations gave the values 410.1 and 409.7 cal./mole for ΔH. The average value, 409.9 ± 0.4 cal./mole was used in the calculation of the entropy change due to the transition.

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

The Entropy of Ammonium Nitrate.—The calculation of the entropy of the salt from calorimetric data is summarized in Table III. The entropy at 15°K. was calculated using the function 6°*D*(192), which best fitted the experimental data to a temperature of 22°K.

TABLE III

THE ENTROPY OF AMMONIUM NITRATE

0–15°K., Debye extrapolation	0.147
15–256.2° (graphical integration)	30.748
Transition, 110.8/256.2	0.433
256.2–298.16°K. (graphical integration)	4.782
Entropy of phase IV at 298.16°K.	36.11 ± 0.05 cal. deg.$^{-1}$ mole^{-1}
298.16–305.4°K. (graphical integration)	0.801
Transition, 409.9/305.4	1.342
305.4–315°K. (graphical integration)	1.057
Entropy of phase III at 315°K.	39.31 ± 0.05 cal. deg.$^{-1}$ mole^{-1}

Standard Free Energy of Formation of Ammonium Nitrate and Standard Entropy of the Aqueous Ammonium Ion.—With the entropy of ammonium nitrate (IV) above, and other entropies given by the National Bureau of Standards in Circular 500,[11] the standard entropy of formation of ammonium nitrate is -145.58 cal. deg.$^{-1}$ mole^{-1}. The standard heat of formation, from Circular 500, is $-87{,}270$ cal. mole^{-1}; the standard free energy of formation of ammonium nitrate (IV) at 298.16°K. consistent with these data is then $-43{,}860$ cal. mole^{-1}.

The value of the entropy of solid ammonium nitrate may be used to calculate another value for the standard entropy of the aqueous ammonium ion at 298.16°K., from data concerning the change in state

$$NH_4NO_3(s) = NH_4^+ + NO_3^-$$

The activity coefficient of ammonium nitrate in its saturated solution, 25.954 *m* at 25°, has been reported as 0.1317 by Wishaw and Stokes,[12] from which $\Delta F^\circ = -1451$ cal. The heat of solution at infinite dilution, according to Circular 500 of the National Bureau of Standards, is 6160 cal. These values give for the standard entropy of solution at 25°, $\Delta S = 25.23$ cal. deg.$^{-1}$. The entropy of the nitrate ion[13] is 25.0 ± 0.3; hence, the standard entropy of the aqueous ammonium ion is 26.6 ± 0.4 cal. deg.$^{-1}$. This result agrees very well with values obtained from three other independent paths.[14]

The free energy of formation of NH_4NO_3 calculated from its standard free energy of solution and the free energies of formation of NH_4^+ and NO_3^- from Circular 500 is $-43{,}960$ cal. The difference between this value and that given above indicates the need for relatively small revisions in Circular 500.

A third independent value for the free energy of formation of ammonium nitrate, which is in excellent agreement with those given above, has been obtained by Mr. George Feick from a study of the dissociation

$$NH_4NO_3(s) = NH_3(g) + HNO_3(g)$$

Torsional Oscillation and Rotation of the Ammonium Ion in Ammonium Nitrate.—For a substance whose lattice is predominantly ionic, such as ammonium nitrate, the nature of the crystalline vibrations may be discerned by consideration of the vibrations permissible for the component ions. The number of internal vibrations of a non-linear complex ion is $3n - 6$, where *n* is the number of atoms in the complex ion. Six degrees of freedom are reserved for translation or rotation of the complex ion as a whole. When the complex ion is part of a crystalline lattice, the three translational modes, and generally the three rotational modes (one about each of the principal axes of the ion), become vibrational modes of the ion as a whole, since translation and rotation are prevented by electrostatic interaction between the ion and other neighboring ions in the crystal. It is useful to maintain the distinction between the three "translational" modes of vibration, which are given the term "lattice vibrations," and the vibrations resulting from frustrated rotation. The latter vibrations are more strictly "torsional oscillations" or "librations" and correspond to incomplete or hindered rotations about each of the three principal axes of the complex ion, resulting in a periodic oscillation about an equilibrium position on the principal axes. At high enough temperatures, the librational motion may become rotational about one or more of the principal axes.

One mole of ammonium nitrate contains 9N atoms, and has associated with it $3(9N) = 6 \cong 27N$ degrees of freedom, which may be assigned as follows

3N, lattice vibrations of NO_3^-
3N, lattice vibrations of NH_4^+
3N, libration or rotation of NO_3^-
3N, libration or rotation of NH_4^+
6N, internal vibrations of NO_3^-
9N, internal vibrations of NH_4^+

The contributions to the heat capacity from excitation of the internal vibrations of the ammonium and nitrate ions are small at low temperatures, and completely negligible below 100°K. The remaining 12 degrees of freedom have been represented with a Debye function (6°) for the lattice vibrations and two Einstein functions (3° each) for the torsional oscillations of the ammonium and nitrate ions. The function

$$6^\circ D(192) + 3^\circ E(340) + 3^\circ(400)$$

represents the experimental results within a few hundredths of a calorie from 15 to 100°K.

The Einstein function with $\theta = 340$, corresponding to a frequency of 236 cm.$^{-1}$, is assumed to be the contribution due to the torsional oscillation of the nitrate ion. This Einstein θ of 340 can be

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(11) National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

(12) B. F. Wishaw and R. H. Stokes, *Trans. Faraday Soc.*, **49**, 27 (1953).

(13) W. M. Latimer, K. S. Pitzer and W. V. Smith, THIS JOURNAL, **60**, 1829 (1938).

(14) C. C. Stephenson, *J. Chem. Phys.*, **12**, 318 (1944).

compared with the values 185, 300, 395 and 256 found to fit the heat capacity curves, respectively, of $TlNO_3$,[15] $AgNO_3$[16] $NaNO_3$[17] and KNO_3[17] from 15 to about 60°K. The single frequency of 236^{-1} cannot have a sharp physical significance because the geometry of the nitrate ion requires at least two different frequencies; nevertheless, it serves a useful purpose in estimating the contribution of the nitrate ion to the total heat capacity.

The onset of torsional oscillation of the ammonium ion requires the addition of the third term, with $\Theta = 400$, corresponding to a frequency of 278 cm.$^{-1}$ This value compares favorably in magnitude with the θ values 560, 482 and 400 for the torsional oscillation of the ammonium ion in ammonium chloride, bromide and iodide, respectively. However, the analysis of the heat capacities was much simpler in the ammonium halides than in ammonium nitrate. The contribution of the nitrate ion to the heat capacity could not be represented satisfactorily above 60°K. in the other nitrates, and the agreement to 100°K. for ammonium nitrate is no doubt fortuitous. The Einstein term with $\Theta = 400$ probably includes some contribution from the nitrate ion as well as the ammonium ion.

This analysis, although approximate in nature, does confirm the fact that both the ammonium and nitrate ions are undergoing torsional oscillations rather than rotations at low temperatures. An analysis at higher temperatures becomes more difficult because the vibrations are anharmonic, the difference between C_p and C_v becomes appreciable, and the internal vibrations are excited. However, the decrease in heat capacity from phase IV to phase III suggests that the ammonium ion is rotating in phase III.

The decrease in heat capacity from phase V to phase IV of 1.63 cal. deg.$^{-1}$ mole^{-1} is of the order of magnitude to be expected from a change in the frequency spectrum for vibrations in the two modifications. The decrease in heat capacity from phase IV to III, 5.3 cal. deg.$^{-1}$ mole^{-1}, is too large to be accounted for in this manner. A reasonable explanation of this large decrease in heat capacity is to attribute three degrees of freedom of rotation in the ammonium ion in phase III, in contrast to fully excited torsional oscillation in phase IV. On this basis, a decrease of $3/2R$ cal. mole^{-1} would be expected. A study of the heat capacity of phase II at lower temperatures, to be presented later, in the form of a solid solution with potassium nitrate, lends support to this hypothesis.

We are indebted to Mr. George Feick, of Arthur D. Little, Inc., for discussions of the thermodynamic properties of ammonium nitrate. This research was assisted by a contribution from the Linde Air Products Division of Union Carbide and Carbon Corporation.

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[15] W. M. Latimer and J. E. Ahlberg, THIS JOURNAL, **54**, 1900 (1932).

[16] W. V. Smith, O. L. I. Brown and K. S. Pitzer, *ibid.*, **59**, 1213 (1937).

[17] J. C. Southard and R. A. Nelson, *ibid.*, **55**, 4865 (1933).

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The Heats, Free Energies and Entropies of Formation of Alkylbenzene–Iodine Complexes

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Values of ΔH, ΔF and ΔS for the interaction of a number of polyalkylbenzenes with iodine in carbon tetrachloride solution have been determined by spectrophotometric methods. In general as ΔH becomes increasingly negative corresponding decreases in ΔF and ΔS values are observed, and these variations are linear. Except for the hexaethylbenzene and *sym*-tri-*t*-butylbenzene complexes the thermodynamic constants become increasingly negative with increasing alkyl substitution of the aromatic donor nucleus. The alkyl groups of hexaethylbenzene must prevent the close approach of the iodine acceptor to the π-electrons of the donor. The complex bond is, therefore, weak, and its formation is accompanied by relatively small entropy changes. Similar, but less marked, steric phenomena influence the stability of the *sym*-tri-*t*-butylbenzene complex.

Values of the order of magnitude of -1 to -2 kcal./mole have been obtained for the heats of formation of iodine complexes of alkylbenzenes and related electron donors.[1-3] The interaction of aromatic compounds with other acceptors such as sulfur dioxide, maleic anhydride, chloranil and polynitro-organic substances in non-polar media are also reported to be mildly exothermic.[4] In no case have marked changes in the heats of complex formation with variations in donor substituents been noted. However these previous investigations have been restricted to a limited series of donors the relative basicities of which, as measured by the equilibrium constants for complex formation, do not vary markedly with a given acceptor.

This report presents data, obtained by ultraviolet spectrophotometric study, concerning the influence of temperature changes on the extent of complex formation in carbon tetrachloride solutions of iodine and a series of alkylated benzenes of rather widely differing donor strengths. It can be shown that the heat and entropy changes which occur in the formation of this series of complexes are related to each other and to the free energy changes in approximately linear fashion.

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[1] T. M. Cromwell and R. L. Scott, THIS JOURNAL, **72**, 3825 (1950).

[2] K. Hartley and H. A. Skinner, *Trans. Faraday Soc.*, **46**, 621 (1950).

[3] C. van de Stolpe, Thesis, "Solvatie van Jodium in Organische Oplosmiddelen," University of Amsterdam, 1953.

[4] See L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954) for a summary.