Williams[27] has recently proposed an equation relating ΔH^0 for complex formation with the ionization potentials of the metal atoms and the radii of the corresponding metal ions. It was not found possible, however, to correlate the data in Table I in this way. Since there are insufficient data to test adequately the equation of Williams with other systems, it cannot be stated whether the chelates of ethylenediaminetetraacetate are abnormal in this respect.

Acknowledgment.—The writer is indebted to Dr. Frank Byrne and his group for the metal ion analyses.

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[CONTRIBUTION FROM ARTHUR D. LITTLE, INC.]

The Dissociation Pressure and Free Energy of Formation of Ammonium Nitrate

BY GEORGE FEICK

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The dissociation pressure and enthalpy of liquid ammonium nitrate have been measured for the temperature range from 190 to 270°. From these data, the free energy and entropy have been calculated for the liquid, and for the solid at 25°. In confirmation of the results of other investigations, the data indicate that the vapor of ammonium nitrate is completely dissociated into NH_3 and HNO_3 in the range of temperatures investigated.

The thermodynamic properties of ammonium nitrate are of interest in connection with the study of its thermal decomposition,[1] especially in the range of temperatures above its melting point (169.6°), for which existing data are not adequate. For this reason, the dissociation pressure has been measured at temperatures up to 250° and the enthalpy of liquid ammonium nitrate has been measured up to 270°. From these data, ΔH and ΔF have been calculated as functions of temperature for the reaction

$$NH_4NO_3(l) \longrightarrow NH_3(g) + HNO_3(g) \qquad (1)$$

on the assumption that the dissociation is complete in the vapor phase.[2] These results were used to calculate the free energy and thence the entropy of molten ammonium nitrate at various temperatures. The resulting entropies were checked against each other by showing that substantially identical results were obtained by reducing each value to 25°. The resulting value is in fair agreement with that calculated from the activities of its ions in aqueous solution.[3] The agreement of these values may be construed as supporting the assumption of complete dissociation of the vapor, as well as the numerical values of the vapor pressure and enthalpy.

Experimental Procedures.—J. T. Baker C.P. ammonium nitrate was used throughout these experiments with no purification other than drying at 110° before use.

Because ammonium nitrate decomposes at an appreciable rate even at temperatures as low as 190°, the method for measuring vapor pressure must be chosen so that the evolved gases (N_2O and H_2O) interfere as little as possible. For this reason, a modified boiling point apparatus was used for the present purpose since the evolved gases are continuously swept away from the zone of measurement. This apparatus was similar to that described by Cottrell[4] except that an iron-constantan thermocouple was used to measure the temperature. The pressure in the system was controlled by a vacuum pump connected through a stopcock and was measured by means of a butyl phthalate manometer (up to 20 mm.) or a mercury manometer (above 20 mm.). It was found necessary to pump continuously on the system during the measurements in order to keep the pressure constant.

Under this latter condition, the measurements are open to the objection that the evolved decomposition products may have had an appreciable effect on the observed pressure. The magnitude of this effect may be estimated with the aid of the following equation

$$P = \left[1 + \frac{3}{2}\left(\frac{\Delta H_v}{Q - \Delta H_r}\right)\right] p \qquad (2)$$

where P is the observed pressure, p is the true dissociation pressure, ΔH_v is the molal heat of dissociation of NH_4NO_3, ΔH_r is the molal heat of decomposition into N_2O and H_2O, and Q is the heat added to the system per mole of NH_4NO_3 decomposed. For the development of this equation, see reference 1.

Since the effect of decomposition is most marked at high temperatures, a check was made of the value of 41 mm. measured at 249.1°. At this temperature, ΔH_v is 38.3 kcal. (see below), and ΔH_r is -14.0 kcal.[1]. Q was estimated as follows: the rate of pressure rise in the apparatus with the stopcock to the vacuum pump closed was 0.233 mm./sec. at a pressure of 41 mm. with 5 g. of NH_4NO_3 in the tube. From the known volume of the apparatus (1550 ml.), the decomposition rate was found to be 7.07×10^{-6} mole/sec. The heating rate was approximated by noting that 4 ml. of water was completely vaporized in 50 sec. from a similar vessel under the same conditions of heating. This corresponds to a heating rate of 0.0476 kcal./sec. Q is then found by dividing the heating rate by the decomposition rate: $Q = 0.0476/7.07 \times 10^{-6} = 6740$ kcal./mole.

Substitution of the above values in equation 2 gives: $P/p = 1.0085$, which indicates that the observed pressure differs from the true dissociation pressure by less than 1%. This difference will be ignored since it is of the same order of magnitude as the error in reading the mercury manometer. For pressure readings at lower temperatures, the error due to thermal decomposition will, of course, be much smaller.

The enthalpy of molten NH_4NO_3 was measured by the method of mixtures in which the molten salt was poured into water contained in a 500-ml. silvered dewar flask. The necessity for jacketing the flask was avoided by choosing the conditions so that the final temperature was near room temperature. Although it is not commonly considered good practice to use this method for materials at temperatures above the boiling point of water, because of the possibility of loss by spattering and vaporization, the method was considered the most practical for the present purpose because the results are not affected by the decomposition of the molten salt, which is very rapid at 270°, and appreciable at lower temperatures. The danger of spattering was mitigated to some degree by using ice-cold water and by the large negative heat of solution of NH_4NO_3. It was found, in fact, that slight spattering occurred only at the two highest temperatures measured.

Another source of error in this procedure was the possibility that the molten nitrate retained some of the water formed by its decomposition. At temperatures above

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(1) G. Feick and R. M. Hainer, THIS JOURNAL, **76**, 5860 (1954).

(2) P. C. Rây and S. C. Jânâ, *J. Chem. Soc.*, **103**, 1565 (1913).

(3) C. C. Stephenson, private communication.

(4) F. G. Cottrell, THIS JOURNAL, **41**, 721 (1919).

220°, this water is probably less than 1%.[5] At lower temperatures, greater amounts of water may be retained, but the reaction is slow and care was taken to avoid keeping the melt hot for long periods of time.

Dissociation Pressure Data.—The observed vapor pressures are given in Table I. The average value of d(ln p)/d($1/T$) corresponds to a heat of vaporization of 39.8 kcal./mole, which is in approximate agreement with the values of 38.5 to 39.1 calculated from thermal data for this temperature range.

TABLE I

DISSOCIATION PRESSURE, FREE ENERGY AND ENTROPY OF DISSOCIATION AND ENTROPY OF AMMONIUM NITRATE

Temp., °C.	Pressure, mm.	$\Delta F_{\text{diss.}}$, kcal./mole	$\Delta S_{\text{diss.}}$, cal./deg. mole	$S_{NH_4NO_3}$ at t, cal./deg. mole	$S_{NH_4NO_3}$ at 25°, cal./deg. mole
188.2	3.25	11.28	60.3	59.2	36.3
205.1	7.45	10.12	60.1	60.3	36.0
215.9	11.55	9.49	59.7	61.1	35.9
223.1	15.80	9.01	59.6	61.8	36.1
236.7	27.0	8.15	59.3	62.7	35.9
249.1	41.0	7.47	58.9	63.8	36.1
				Best value	36.0

Enthalpy Data.—The data leading to the enthalpy of molten NH_4NO_3 are summarized in Table II. In making the calculations, the heat of solution data were taken from the National Bureau of Standards Tables[6] and the specific heats of aqueous NH_4NO_3 solutions were taken from Gmelin.[7]

The resulting values of enthalpy are plotted against temperature in Fig. 1. The data appear to be precise to about ±100 cal. and are represented within their precision by a straight line whose slope corresponds to a heat capacity of 38.5 cal./mole deg. Extrapolation to the melting point gives an enthalpy of 8.15 kcal./mole for liquid NH_4NO_3 at 169.6°, based on the solid (IV) at 25°.

TABLE II

ENTHALPY OF LIQUID AMMONIUM NITRATE

Temperatures, °C.			Weights, g.		Enthalpy above 25°, kcal./mole
NH_4NO_3	Water	Mixture	NH_4NO_3	Water[a]	
185.5	1.12	29.1	178.4	302.6	8.72
190.25	1.74	11.72	65.9	302.1	9.00
211.27	1.76	13.65	65.0	294.5	9.74
217.51	2.16	15.24	69.8	304.3	9.95
227.36	1.56	15.52	68.2	300.3	10.49
240.54	1.60	26.85	109.8	297.9	10.91
269.14	1.92	14.56	49.1	301.0	11.95

[a] The effective heat capacity of the calorimeter was found by measurement to be equivalent to 19.5 g. of water.

Heat of Dissociation.—The above data were used to calculate ΔH for reaction 1 at various temperatures. The enthalpies for the reactants at 25° were taken from the Bureau of Standards Tables[6] and the enthalpies of the products at higher temperatures from Kelley.[8] Since the enthalpy of nitric acid vapor is given only to 500°K., graphical extrapolation was made for the higher temperatures. The results are given in Table III.

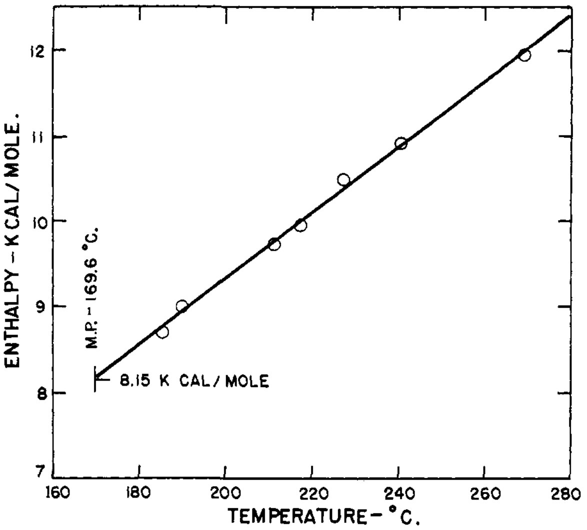

Fig. 1.—Enthalpy of liquid NH_4NO_3 based on solid (IV) at 25°.

TABLE III

HEAT OF DISSOCIATION OF AMMONIUM NITRATE

Temp., °C.	169.6	200	250[a]	300[a]	350[a]
ΔH, kcal./mole	39.33	38.92	38.25	37.65	37.12

[a] Based on extrapolated values for the enthalpy of HNO_3 (g).

Free Energy and Entropy Calculations.—The free energy of dissociation was calculated from the dissociation pressure at each of the observed temperatures by means of the relation

$$\Delta F = -RT \ln K = -RT \ln \frac{p^2}{4} \qquad (3)$$

where p is the dissociation pressure in atmospheres. From these values, the entropy of dissociation was found, using the equation

$$\Delta F = \Delta H - T\Delta S \qquad (4)$$

and the previously calculated values of ΔH.

The absolute entropy of ammonium nitrate at each of the above temperatures was calculated, using the entropy values for ammonia and nitric acid given by Kelley.[8] Values for the latter substance above 500°K. were found by extrapolation. The results of the foregoing calculations are summarized in Table I.

The data may be checked for internal consistency by reducing the absolute entropy values to a common temperature, which was chosen as 25°. The transition temperatures and heats of transition for the various solid forms of ammonium nitrate were taken from the Bureau of Standards Tables.[6] The heat capacities used in the calculation are summarized in Table IV, together with the sources from which they were taken. The value of 45.6 kcal./mole for c, I was found by difference from the measured enthalpy of the liquid. Although the accuracy of this value is undoubtedly poor, its effect on the over-all entropy calculation is small.

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(5) "Gmelins Handbuch der anorganischen Chemie, 8 Aufl. System Nummer 23: Ammonium. Lieferung I," Verlag Chemie, Berlin, 1936, p. 123.

(6) "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards, 500, 1952.

(7) Reference 5, p. 124.

(8) K. K. Kelley, Bureau of Mines Bulletin 476.

TABLE IV

HEAT CAPACITY DATA

Form	C_p, cal./mole, °C.	Source
c, IV	33.6	Ref. 8
c, III	28.4	Ref. 9
c, II	34.1	Ref. 9
c, I	45.6	See text
Liq.	38.5	This work

The resulting values for the entropy are given in Table I and are in good agreement except for the value at 188.2°. The best value for the absolute entropy of ammonium nitrate at 25° may be taken as 36.0 cal./mole °C. The agreement of these values confirms the assumption that the vapor of ammonium nitrate is completely dissociated in the range of temperature investigated.

The value of entropy obtained by this method (36.0 e.u.) may be compared with the value of 36.11 obtained by Stephenson from low-temperature calorimetric data.[3]

From the entropy and heat of formation the standard free energy of formation of ammonium nitrate is found to be −43.82 kcal./mole.

The author takes pleasure in acknowledging the continuing advice and criticism of Dr. Clark C. Stephenson of Massachusetts Institute of Technology during the course of this work.

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[CONTRIBUTION FROM ARTHUR D. LITTLE, INC.]

On the Thermal Decomposition of Ammonium Nitrate. Steady-state Reaction Temperatures and Reaction Rate

BY GEORGE FEICK AND R. M. HAINER

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When ammonium nitrate is heated, it decomposes exothermically into nitrous oxide and water. At the same time, it dissociates endothermically into ammonia and nitric acid vapor. As a result of these two concurrent reactions, the molten mass of nitrate tends to reach a steady-state temperature, which is a function of the ambient pressure and of the heating rate. At pressures near atmospheric, the reaction is thus limited to rates which are very slow compared to those of explosive reactions. An equation has been derived relating the temperature to the above variables, which is in good agreement with experiment over the limited range of conditions studied. The constant temperature reaction has been applied to the measurement of reaction rate.

Although it is well known that ammonium nitrate decomposes exothermically when heated, giving N_2O and H_2O, its behavior on heating is not typical of an exothermic reaction, in that in small quantities it usually shows little tendency toward self-accelerating decomposition, or even toward continued reaction after the source of heat is removed.[1] Sherrick[2] failed to cause an explosion of unconfined NH_4NO_3, even by bringing it into contact with molten iron from the "thermit" reaction. On the other hand, Herquet[3] has shown that suitably confined NH_4NO_3 is capable of rapid, self-accelerating decomposition at initial temperatures of 260 to 280°.

The present paper offers an interpretation of such observations by showing that molten, decomposing ammonium nitrate tends to seek a definite and predictable limiting temperature which is a function of the external pressure and of the heat supplied to, or removed from the molten mass by its surroundings. This limitation of temperature is the result of the endothermic dissociation of NH_4NO_3 into gaseous NH_3 and HNO_3, a reaction which, under the steady-state temperature conditions, absorbs all the heat available from the decomposition. At pressures near atmospheric, and in the absence of externally supplied heat, the reaction is limited to temperatures at which the decomposition occurs with easily measurable velocity. When heat is added, even from a very hot source, the temperature of the NH_4NO_3 is limited by its own dissociation, to values at which the decomposition rate is still comparatively moderate. At higher pressures, however, dissociation is repressed and the temperature can rise until an explosive rate of decomposition is attained. The application of these results to the question of the explosion hazard of ammonium nitrate will be discussed in more detail by Hainer.[4]

Steady-state Reaction Temperature.—The main reactions of interest are irreversible decomposition

$$NH_4NO_3(l) \longrightarrow N_2O(g) + 2H_2O(g) \qquad (1)$$

and reversible dissociation

$$NH_4NO_3(l) \rightleftharpoons NH_3(g) + HNO_3(g) \qquad (2)$$

Saunders[5] has shown that reaction 1 accounts for 98% of the irreversible decomposition of NH_4NO_3 in the temperature range 230 to 260°. The side reactions will be considered negligible for the present purpose. The enthalpy change for this reaction

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(1) G. Feick and R. M. Hainer, *Nature*, **173**, 1188 (1954).

(2) J. L. Sherrick, *Army Ordnance*, **4**, 237 (1924).

(3) M. L. Herquet, *Explosifs*, **5**, 29 (1952).

(4) R. M. Hainer, "The Application of Kinetics to the Hazardous Behavior of Ammonium Nitrate." Paper presented to the Fifth International Symposium on Combustion, August, 1954. R. M. Hainer and W. C. Lothrop, "Thermal Hazard in Ammonium Nitrate and High-Percentage Ammonium Nitrate Materials," presented to the Division of Industrial and Engineering Chemistry, Section C, American Chemical Society, September, 1954.

(5) H. L. Saunders, *J. Chem. Soc.*, **121**, 698 (1922).