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

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

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).

may be estimated from published data,[6–8] and is given at various temperatures in Table I.

TABLE I

CALCULATED ΔH FOR THE REACTION: $NH_4NO_3(l) \rightarrow N_2O(g) + 2H_2O(g)$

Temp., °C.	169.6	200.0	250.0	300.0
ΔH, kcal./mole	−13.21	−13.53	−14.03	−14.58

The dissociation pressure and heat of dissociation for reaction 2 have been discussed by Feick.[8] For temperatures above 250°, the dissociation pressure (p) has been estimated from free energies based on extrapolation of Kelley's[7] values for the enthalpy and entropy of nitric acid vapor. It is found that the results are represented within the accuracy of the calculation from 250 to 350° by the empirical equation

$$\log_{10} p \text{ (cm.)} = -4109/T + 8.502 \qquad (3)$$

which is plotted in Fig. 1 as the curve of dissociation pressure.

The temperature-regulating relationship may be derived by considering a mass of molten NH_4NO_3 at an arbitrary temperature and pressure, and allowing a differential amount, dN_r moles, to decompose according to reaction 1. The gaseous N_2O and H_2O, saturated with NH_3 and HNO_3, are removed from thermal contact with the remaining liquid. Let ΔH_r and ΔH_v represent the enthalpy changes per mole due to reactions 1 and 2, respectively. Let dN_v represent the number of moles of NH_4NO_3 dissociated during the decomposition and dQ the heat added to the mass from external sources during the same interval of time. The heat balance may then be written

$$dQ - (\Delta H_r)(dN_r) - (\Delta H_v)(dN_v) = dq \qquad (4)$$

where dq is the net heat produced in the melt. If dq is positive, the temperature of the melt will rise, its dissociation pressure will increase, and dN_v will therefore increase for a given value of dN_r until dq approaches zero. If dq is negative, the temperature will fall until dq again approaches zero, the ultimate temperature being the same in both cases. The above argument is restricted to values of dq greater than (ΔH_r) (dN_r). If dq is less than this value, the rate of heat loss is greater than its rate of production and the mass will cool until reaction ceases.

For this steady-state temperature condition, it is convenient to rewrite the above in integrated form and on the basis of one mole of ammonium nitrate decomposing to N_2O and water. N_v is defined as the ratio of the amount in moles of NH_4NO_3 dissociated to the amount decomposed, and Q as the heat added per mole of NH_4NO_3 decomposed. Since dq becomes zero for the steady state, the heat balance becomes

$$Q - \Delta H_r - (N_v)(\Delta H_v) = 0 \qquad (5)$$

or solving for N_v

$$N_v = \frac{Q - \Delta H_r}{\Delta H_v} \qquad (6)$$

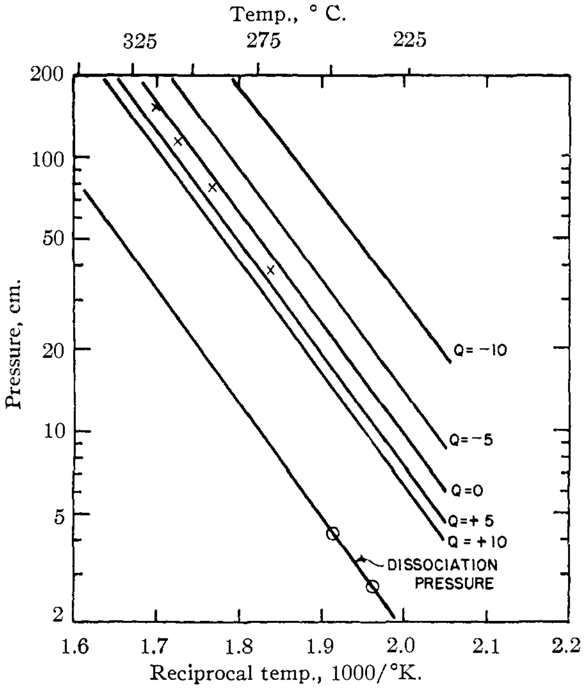

Fig. 1.—Relations between steady-state temperature and pressure: X, experimental points for $Q = 0$; O, measured dissociation pressure.[8]

The same quantity may also be calculated by assuming that the evolved gases are saturated with the dissociation products and that the ideal gas laws apply

$$N_v = \frac{3}{2}\left(\frac{p}{P - p}\right) \qquad (7)$$

where p is the vapor pressure of the dissociation products at the steady-state temperature and P is the total pressure or ambient pressure on the reacting mass.

Equating expressions 6 and 7 and solving for P, gives

$$P = \left[1 + \frac{3}{2}\left(\frac{\Delta H_v}{Q - \Delta H_r}\right)\right] p \qquad (8)$$

From this it is evident that except for small changes of ΔH_v and ΔH_r with temperature, the total pressure P is proportional to the dissociation pressure p. The proportionality factor is a function of Q. Conversely, it is evident that determination of P and Q is necessary and sufficient to determine the dissociation pressure p and, therefore, to define the temperature of the melt. These relationships are shown in Fig. 1, in which the dissociation pressure p and the total pressure P, at various values of Q are shown as functions of temperature.

It is interesting to note that when the decomposition rate is small compared to the rate of heat input, Q becomes large and the dissociation pressure approaches the total pressure, as is evident from examination of eq. 8. It is also noteworthy that the equation is discontinuous when $Q = \Delta H_r$. The physical interpretation of this is that when Q becomes more negative than ΔH_r, the mass will cool off until the reaction stops. As a practical matter, Q may be estimated for a given reaction with the aid of Fig. 1, from measurements of the total

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(6) "Selected Values of Chemical Thermodynamic Properties," U. S. National Bureau of Standards, 1947.

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

(8) G. Feick, THIS JOURNAL, 76, 5858 (1954).

pressure and the steady-state temperature of the reacting mass.

This relationship has been tested experimentally for the adiabatic case ($Q = 0$) by measuring the steady-state temperature at pressures ranging from 38 to 152 cm. The results are shown in Table II, and as the experimental points in Fig. 1. The difference between the observed and calculated curves may be due to neglect of side reactions accompanying the decomposition and to failure to obtain perfectly adiabatic conditions in the experiments. The agreement, however, appears to be sufficiently close to confirm the validity of the general approach in the range of temperatures covered by the experiments. In applying this relationship at higher temperatures, it should be remembered that the side reactions leading to products such as NO and N_2 probably become more important with increasing temperature, and that such reactions are generally more exothermic than reaction 1. This indicates that the limiting temperatures may in fact be somewhat higher for a given pressure than eq. 8 would indicate.

TABLE II

STEADY-STATE TEMPERATURE *vs.* PRESSURE FOR ADIABATIC CONDITIONS

Total pressure, cm.	Temp., °C. Calcd.	Temp., °C. Measured
38	266	271
76	289	292
114	304	306
152	314	315

If carbonaceous or other combustible materials are present with the molten nitrate, both added heat of combustion and increased evolution of gas will affect the limiting temperature. It is difficult to write a relevant quantitative relation in this case, however, since the molten nitrate partially quenches the combustion and leads to irregular reaction rates and indeterminate products.

Decomposition Rate.—The constant temperature reaction may conveniently be used in the experimental determination of the rate constant for reaction 1. To perform this experiment, it is only necessary to place molten ammonium nitrate in an insulated vessel, which is weighed at suitable intervals after the steady-state temperature has been attained. The results of such an experiment, at one atmosphere and 290°, are given in Table III. The over-all rate constant given in this table is a measure of the combined loss of NH_4NO_3 through decomposition and through evaporation from the melt by dissociation. The decrease of the observed over-all rate constant with time is probably due chiefly to recondensation of some of the dissociation products during the later stages of the reaction, when the liquid level had dropped low in the container. If this interpretation is true, the initial values of Table III are probably more nearly correct than later ones. It may therefore be surmised that the true value of the over-all constant is somewhat greater than 2.3×10^{-3} sec.$^{-1}$.

The rate constant for reaction 1 may be found from the above over-all constant by correcting for the NH_4NO_3 lost by evaporation from the melt.

TABLE III

OVER-ALL[a] DECOMPOSITION RATE OF NH_4NO_3 AT 290°

Time, sec.	Remaining NH_4NO_3, g.	Over-all rate constant, sec.$^{-1}$
0	190	....
48	170	2.32×10^{-3}
101	150	2.36×10^{-3}
163	130	2.31×10^{-3}
236	110	2.29×10^{-3}
327	90	2.20×10^{-3}
446	70	2.11×10^{-3}
523	60	2.00×10^{-3}
626	50	1.77×10^{-3}

[a] Not corrected for dissociation of NH_4NO_3.

At 290°, the dissociation pressure is found from eq. 3 to be 16.1 cm. From this value, N_v, the number of moles of NH_4NO_3 vaporized per mole decomposed, is found to be 0.403 by eq. 7. The corrected rate constant is therefore

$$2.3 \times 10^{-3}/1.403 = 1.64 \times 10^{-3} \text{ sec.}^{-1} \quad (9)$$

at 290°.

This value may be compared with the results of Robertson,[9] who gives the equation

$$K = 10^{13.8} e^{-40,500/RT} \quad (10)$$

The rate constant at 290° calculated from this equation is 12.6×10^{-3} sec.$^{-1}$, or some 7.5 times larger than the constant above. Robertson indicates, however, that his experiments may give high results because of evaporation of ammonium nitrate. Since the present value is probably low, because of recondensation of NH_4NO_3, the true value for the rate constant at 290° undoubtedly falls within the limits of the above figures.

Experimental

J. T. Baker C.P. NH_4NO_3 (stated Cl content = 0.0001%) was used without purification, other than drying at 110°.

A. **Steady-state Temperatures.**—The ammonium nitrate was placed in a glass reaction bulb of about 200-ml. capacity. This bulb was provided with a thermocouple well, in which was inserted an iron–constantan thermocouple, connected to a recording potentiometer. The reaction bulb was surrounded with a heating jacket, consisting of a brass tube wrapped with asbestos paper and nichrome ribbon. The heating jacket was supplied with current from a continuously variable transformer. The bulb and jacket were contained in a 500-ml. silvered Dewar flask, the mouth of which was packed with glass wool. The evolved vapors pass into the air-cooled trap of 250-ml. capacity. The pressure in the system was measured by a mercury manometer, and was controlled by stopcock, which was connected to an aspirator, if the desired pressure was below atmospheric.

In each experiment, the heating jacket was energized and allowed to rise to a temperature near the predicted value. At this point, the current was reduced to a value which had previously been found just sufficient to compensate for the heat losses at that temperature. The temperature of the nitrate rose sharply, leveled off at a temperature determined by the external pressure, and remained constant until the decomposition was complete. Minor changes in the temperature of the heating jacket had little effect on the equilibrium temperature of the melt.

At 271° ($^1/_2$ atm.), the temperature remained constant for about 20 minutes, with an initial charge of about 60 g. of NH_4NO_3. At 315° (2 atm.), however, an initial charge of 100 g. was consumed in 2–3 minutes. It is noteworthy that the reaction at 315° was perfectly smooth and regular, and that the brown color of higher oxides of nitrogen was not noticeable in the product gases (*cf.* reference 5).

It was found that the evolved vapors could be ignited by

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(9) A. J. B. Robertson, *J. Soc. Chem. Ind.*, **67**, 221 (1948).

strongly heating the tube leading from the reaction vessel. The resulting flame was yellow-brown in color and could be held in place by a constriction in the tube. This flame is undoubtedly caused by the oxidation of ammonia by nitric acid vapors, together with the decomposition of N_2O. The brown color of NO_2 was evident in the products. In one experiment, the flame flashed back through the constriction to the surface of the NH_4NO_3 in the reaction vessel. The evolved gases burned quietly at the surface of the melt until the nitrate was consumed.

B. **Reaction Rate.**—The reaction rate was measured by preheating a 500-ml. silvered Pyrex dewar flask to about 275°, by means of an inserted electric heater. When the required temperature had been attained, the heater was removed, 300 g. of molten NH_4NO_3 at approximately the same temperature was added, and the flask was loosely closed with an insulated glass cover through which a mercury thermometer was inserted into the melt. The entire assembly was placed on a platform balance and weighed at suitable intervals.

Over an interval of about 3 minutes, during which time 110 g. of NH_4NO_3 was consumed, the temperature rose to 290° (corrected for stem exposure) and leveled off. This temperature is somewhat lower than the 292° reported in Table II because of heat loss from the dewar flask. The temperature remained steady for about ten minutes, at the end of which time only about 50 g. of nitrate remained. Dense clouds of white fume were evolved during the reaction, as a result of dissociation and recombination of NH_4NO_3. The loss in weight of the flask during the constant temperature reaction is given in Table III, together with the calculated values of the over-all rate constant, which includes the NH_4NO_3 lost by vaporization.

The authors take pleasure in acknowledging the advice and coöperation of Dr. Alfred G. Emslie and Dr. William E. Gordon.

This work was performed, in part, under the auspices of the United States Coast Guard and the Advisory Committee on Hazards of Ammonium Nitrate Transportation of the National Research Council. Permission to publish this article has been granted by the United States Coast Guard, but neither of the sponsoring agencies necessarily approves the technical opinions or conclusions therein expressed.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Dissociation of Fluoborate Ion in Anhydrous Hydrofluoric Acid[1,2]

BY MARTIN KILPATRICK[3] AND FRED E. LUBORSKY

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In a previous paper, the equilibrium constants for the reaction $Ar + HF \rightleftarrows ArH^+ + F^-$ were reported for the methylbenzenes and shown to vary from 10^{-8} to 10^{-2}. When sufficient boron trifluoride was introduced into the system, it was shown that essentially all of the aromatic was converted to the aronium ion and it was assumed that the addition of BF_3 established a second equilibrium $F^- + BF_3 \rightleftarrows BF_4^-$. Further support for the existence of this equilibrium and the calculation of this equilibrium constant are the subjects of the present paper. This constant has been evaluated from conductance studies on potassium fluoride and potassium fluoborate, and from the change in conductance of potassium fluoride on addition of boron trifluoride. Both methods give a value approximating 2×10^2 at 20°, or 5×10^{-3} for the dissociation of the fluoborate ion.

In an earlier paper[4] the equilibrium constants were reported for the reaction

$$Ar + HF \rightleftarrows ArH^+ + F^- \quad (1)$$

where Ar represented benzene or a methylbenzene. It was also shown that reaction 1 could be displaced to the right by the addition of a fluoride acceptor such as boron trifluoride

$$F^- + BF_3 \rightleftarrows BF_4^- \quad (2)$$

The existence of such an equilibrium is shown by means of conductance studies on potassium fluoborate and potassium fluoride in the solvent anhydrous hydrofluoric acid, and conductance and vapor pressure studies on the addition of boron trifluoride to potassium fluoride.

Figure 1 gives the specific conductance of potassium fluoride on addition of boron trifluoride and the curves are analogous to those reported in the previous paper[4] for the addition of boron trifluoride to solutions of certain of the methylbenzenes, namely, mesitylene, isodurene, pentamethylbenzene and hexamethylbenzene. The interpretation of the decrease in specific conductance on addition of boron trifluoride is that the fluoride ion is replaced by the less mobile fluoborate ion. This is substantiated by the curves of the total vapor pressure of these same solutions as shown in Fig. 2. The curves indicate almost complete reaction of

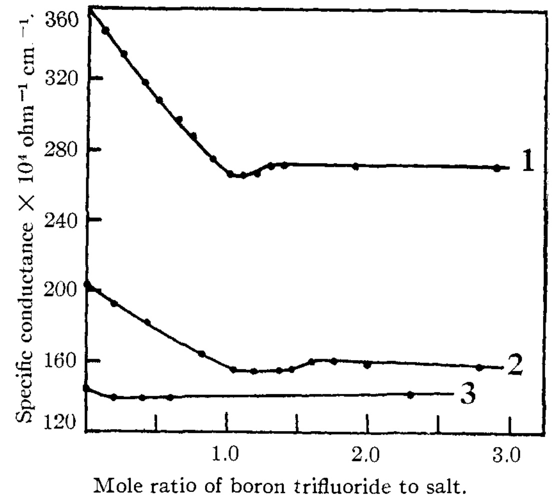

Fig. 1.—The conductance of salts in anhydrous hydrofluoric acid on the addition of boron trifluoride: 1, 0.104 *m* KF; 2, 0.0512 *m* KF; 3, 0.0447 *m* KBF_4.

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[1] Abstracted in part from the Ph.D. thesis of Fred E. Luborsky, Illinois Institute of Technology, June, 1952.

[2] Presented before the Division of Physical and Inorganic Chemistry at the 125th Meeting of the American Chemical Society, Kansas City, April, 1954.

[3] Fulbright Research Scholar in 1953 at the Royal Veterinary and Agricultural College, Copenhagen, Denmark.

[4] M. Kilpatrick and F. E. Luborsky, THIS JOURNAL, **75**, 577 (1953).