

[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES]

Heats and Entropies of Reaction of Metal Ions with Ethylenediaminetetraacetate*

BY ROBERT G. CHARLES

RECEIVED JUNE 17, 1954

Heats of reaction of a series of monovalent and divalent metal ions with the ethylenediaminetetraacetate ion in aqueous solution have been determined by a direct calorimetric method. From these values and published equilibrium constants, the corresponding entropy changes have been calculated. Much of the high stability associated with many of the ethylenediaminetetraacetate chelates has been found to be due to the high positive values of ΔS^0 for these reactions. A relationship between the observed ΔS^0 values and the standard partial molal entropy of the metal cation is pointed out. ΔH^0 values for the reactions have been found to be a function of the electronegativity, size and charge of the metal cation.

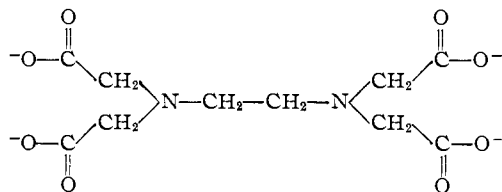
Although solution equilibria between metal ions and chelating ions or molecules have been rather extensively studied in recent years,¹ comparatively few values are available for the heat content changes accompanying such reactions. Such values are of considerable interest in that they are more closely related to the metal-ligand bond strengths in the metal chelates than are the equilibrium constants for the same reaction.² In addition, a knowledge of the heat content changes for such reactions, together with the corresponding equilibrium constants, permit the calculation of the entropy changes for these reactions.

Most of the ΔH values which have been reported for chelate formation have been determined from the variation of $\log K$ (where K is the stability constant) with temperature. Because of the limited temperature range available, together with the frequently observed small variation of $\log K$ with temperature, the values obtained are not always accurate.^{3,4} In the present work, a direct calorimetric method has been adopted for determining the heats of reaction between a series of metal ions and the ethylenediaminetetraacetate ion in water solution. Ethylenediaminetetraacetate was chosen for study for two reasons. First, it forms stable chelates of considerable water solubility with a large number of metal ions; and secondly, equilibrium constants are available for the formation of many of these.^{5,6}

The specific reaction studied was



where M^{+Z} is the metal cation, $Z = 1$ or 2 , and Y^{-4} is the ion



ΔH for the reaction, as studied, differs from that at infinite dilution (ΔH^0) only by the differences in heats of dilution of the products and of the react-

ants, a quantity which can be taken to be negligible for solutions as dilute as those used here. The general procedure adopted for the divalent metals involved measuring the heat of reaction between the metal ion and an aqueous solution of the tetrasodium salt of ethylenediaminetetraacetic acid. Two series of experiments were made, one with an equivalent amount of the tetrasodium salt (or a small excess) and the other with a two-fold excess (with respect to the metal ion employed). Since, under the conditions of the determinations, part of the ethylenediaminetetraacetate is complexed with sodium ions⁷ to give NaY^{-3} , it was necessary to determine ΔH^0 for the reaction between Na^+ and Y^{-4} in order to correct to ΔH^0 values corresponding to reaction 1. This was done by measuring the heat of reaction between ethylenediaminetetraacetic acid (H_4Y) dissolved in an excess of aqueous tetramethylammonium hydroxide and sodium chloride. The tetramethylammonium ion is too large to form a chelate of significant stability, so that ΔH^0 for this reaction corresponds to reaction 1, with $M^{+Z} = Na^+$. ΔH^0 for this reaction was then used to correct the values obtained using the tetrasodium salt. The heat of reaction for the Li^+ ion was obtained in the same manner as for the sodium ion, using $LiCl$, H_4Y , and tetramethylammonium hydroxide.

Experimental

Reagents.—Reagent grade disodium salt of ethylenediaminetetraacetic acid dihydrate was used as obtained from the supplier (Bersworth Company, Framingham, Mass.). Ethylenediaminetetraacetic acid was prepared by acidifying a water solution of the pure disodium salt with hydrochloric acid, filtering and washing the precipitate, and drying the precipitate at 110° . A sample of relatively pure ethylenediaminetetraacetic acid was also used as obtained from the Glyco Products Company of Brooklyn, New York. Results obtained using the two samples of acid were identical within experimental error.

Metal ion solutions containing approximately one mole of metal salt/l. were prepared from reagent grade nitrates and distilled water. In the cases of barium, sodium and lithium, the chlorides were used. The metal ion solutions were standardized by conventional methods. The standard aqueous $0.2 M$ NaOH solution employed was carbonate free. Aqueous solutions of Na_4Y were prepared as needed by adding an equivalent amount of NaOH solution to a weighed amount of Na_2H_2Y and diluting with distilled water. It was necessary to adopt this procedure because of the difficulty encountered in purifying the solid tetrasodium salt.

Apparatus and Procedures.—A simple adiabatic calorimeter was employed consisting of a silvered Dewar flask of about 500-ml. capacity and equipped with a 45/50 F joint, a combination glass top and stirring tube (fashioned from a 45/50 F inner Pyrex joint and 2-mm. capillary

* Presented at the National Meeting of the American Chemical Society, New York, September, 1954.

(1) For a summary of such data, see A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952.

(2) A. R. Burkin, *Quart. Rev.*, **5**, 1 (1951).

(3) F. Basolo and R. K. Murmann, *THIS JOURNAL*, **76**, 211 (1954).

(4) J. W. Cobble, *J. Chem. Phys.*, **21**, 1451 (1953).

(5) V. L. Hughes and A. E. Martell, *J. Phys. Chem.*, **57**, 694 (1953).

(6) F. F. Carini and A. E. Martell, *THIS JOURNAL*, **76**, 2153 (1954).

(7) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

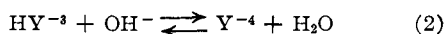
tubing), a sample tube, and a Beckmann thermometer. Stirring was accomplished by a stream of nitrogen through the stirring tube. The nitrogen was first bubbled through alkaline pyrogallol and then through a bubbler, filled with water, and placed in a constant temperature bath maintained at $25 \pm 0.01^\circ$. The calorimeter proper was placed in the same bath during a run. The sample tube, of approximately 15-ml. capacity, consisted of a glass bulb with a small opening at the bottom and a narrower tube extending from the top of the bulb through the top of the calorimeter. In practice, the bottom opening was plugged with paraffin and the metal ion solution was pipetted into the bulb. During a run the paraffin seal was broken by means of a glass rod extending through the tube of the sample holder.

For a run the apparatus was assembled with about 200 ml. of the tetrasodium salt solution (containing either 0.01 or 0.02 mole of Na_4Y in a known weight of water and adjusted to $25 \pm 2^\circ$) in the Dewar flask and 10 ml. of the metal ion solution in the sample holder. The calorimeter was placed in the constant temperature bath and stirring started. After coming to thermal equilibrium, temperature-time readings were taken over a period of 15 or 20 minutes. The metal ion solution was then added and temperature time readings again taken until the rate of temperature change with time again became constant. In all cases, the reaction appeared to be complete within a few minutes. Runs with lithium or sodium ions were performed in the same manner as above, except that the solution in the Dewar consisted of one equivalent (with respect to the metal ion) of H_4Y dissolved in an aqueous solution containing 50 g. of a 10% solution of tetramethylammonium hydroxide (an excess).

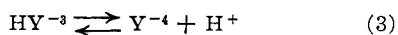
The heat capacity of the calorimeter was determined by calibration, using the heat of reaction of HClO_4 with NaOH , and of H_2SO_4 with NaOH .⁸ Values for the heat capacity obtained with the two reactions agreed to within 1%.

Results obtained with the calorimeter were corrected for differences in specific heat, using values determined by independent measurements of this quantity on typical solutions. Such corrections were small (1% or less of the measured value). The results were also corrected for the heats of dilution of the metal salts. The heat of dilution of the tetrasodium salt was found to be negligible for the present purposes.

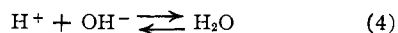
Calculations.— ΔH^0 for each of the reactions was calculated in the usual fashion from the observed temperature change (corrected for heat leakage) and the number of moles of metal ion employed, applying the corrections mentioned above. One additional correction is necessary. Since the fourth hydrogen of H_4Y is only weakly acidic,¹⁰ a solution of the tetrasodium salt is partially hydrolyzed; that is, the solution contains some HY^{-3} in addition to the Y^{-4} and NaY^{-3} . When metal ion is added, the HY^{-3} is either partially or completely reconverted to Y^{-4} as the Y^{-4} originally present in solution combines with the metal ion. Thus, a heat effect due to the reaction



is superimposed on the heat of reaction of the metal ion with Y^{-4} . From the value of ΔH^0 for the reaction¹⁰



and ΔH^0 for



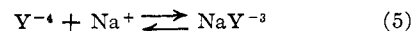
ΔH^0 for reaction 2 is calculated to be -8.5 kcal./mole. From the ionization constant of HY^{-3} at

(8) Calculated from values given in reference 9.

(9) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, 1952.

(10) F. F. Carini and A. E. Martell, *TETRA JOURNAL*, **75**, 4810 (1953).

the ionic strength of the present runs,¹¹ the water constant, and the equilibrium constant for the reaction⁷



the amount of HY^{-3} present at the lower concentration of tetrasodium salt is found to be 1.4% of the total Na_4Y . This corresponds to a correction of $+0.1$ kcal./mole to be added to the experimentally determined values. The correction at the higher concentration of Na_4Y was found to be negligible.

The equilibrium formation constants⁵⁻⁷ of all the chelates studied, with the exception of that for the sodium complex, are sufficiently large that reaction 1 can be considered to proceed to completion under the conditions used here. Using the formation constant for the sodium complex⁷ this reaction was found to be 51% complete under the conditions of the sodium ion determination, 88% complete with one equivalent of Na_4Y , and 94% complete with two equivalents. The appropriate factor was used in correcting the values obtained under these sets of conditions.

Values of ΔS^0 were calculated from the equation

$$\Delta F^0 = \Delta H^0 - T \Delta S^0 \quad (6)$$

where ΔF^0 was either obtained from the literature⁶ or calculated from reported values of $\log K$, using the relation

$$\Delta F^0 = -2.303RT \log K \quad (7)$$

Where $\log K$ is reported for a temperature other than 25° , the value at 25° was calculated using the equation

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{T^2} \quad (8)$$

Thermodynamic values of $\log K$ are available only for the alkaline earth chelates⁶ or Y^{-4} . In the case of the other metals, approximate values of ΔF^0 were calculated from the concentration constants reported by Hughes and Martell⁵ and by Schwarzenbach.⁷ A value of $\log K$ for the Mn chelate, consistent with the values used for the other complexes, was estimated from $\log K$ as given by Schwarzenbach¹² by comparing the values given by him¹² and by Hughes and Martell⁵ for other transition metal chelates.

Values for ΔH^0 , ΔF^0 and ΔS^0 are given in Table I. For reasons given below, ΔS^0 is calculated only from ΔH^0 values obtained using one equivalent of Y^{-4} .

Discussion

It will be observed from Table I that while there is general agreement between the values of ΔH^0 obtained under the two sets of experimental conditions, the values obtained with two equivalents of Y^{-4} are slightly the more negative. This difference, if real, may indicate some small tendency toward side reactions in the presence of excess Y^{-4} , such as the formation of hydroxy complexes or the reaction of one metal ion with more than one Y^{-4} ion. Since such side reactions would be minimized when no excess of Y^{-4} is present, the values in column 3 may

(11) F. F. Carini and A. E. Martell, *ibid.*, **74**, 5745 (1952).

(12) G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 576 (1951).

be the more reliable and have, therefore, been used to calculate ΔS^0 . It should be pointed out, however, that the values of ΔS^0 would not be greatly different if the data in column 4 had been used.

TABLE I
THERMODYNAMIC DATA AT 25° FOR THE REACTION
 $M_{aq}^{+Z} + Y_{aq}^{-4} \rightleftharpoons MY_{aq}^{-4+Z} + xH_2O$

Metal ion	ΔF^0 ,	ΔH^0 , kcal./mole		ΔS^0 , e.u.
	kcal./mole	1 equiv. Y^{-4}	2 equiv. Y^{-4}	
Cu ⁺⁺	-24.4	-8.2	-8.4	+55
Ni ⁺⁺	-24.0	-7.6	-7.8	+55
Co ⁺⁺	-21.4	-4.1	-4.7	+58
Mn ⁺⁺	-17.2	-5.2	-5.7	+41
Zn ⁺⁺	-20.9	-4.5	-4.9	+55
Cd ⁺⁺	-20.5	-9.1	-9.3	+38
Pb ⁺⁺	-23.6	-13.1	-13.4	+35
Mg ⁺⁺	-12.40	+3.1	+3.1	+52
Ca ⁺⁺	-14.97	-5.8	-6.5	+31
Sr ⁺⁺	-11.90	-4.2	-4.2	+26
Ba ⁺⁺	-10.54	-5.1	-5.3	+18
Na ⁺	- 2.3	-1.4		+ 3
Li ⁺	- 3.8	+0.1		+13

Since this work was begun, Carini and Martell⁶ have reported ΔH^0 values corresponding to reaction 1 with $M^{+Z} = Mg^{++}, Ca^{++}, Sr^{++}$ and Ba^{++} . The values obtained were -2.9, -2.5, -4.1 and -4.1 kcal./mole. These data were obtained by a study of the temperature variation of the corresponding equilibrium constants. With the possible exception of the value for Mg^{++} , experimental errors are probably sufficient to account for the differences between these data and the values reported in Table I. It is recognized that ΔH^0 values obtained by the temperature variation method are sensitive to small experimental errors,^{3,4} particularly when such ΔH^0 values are small. In the case of magnesium, there appears to be little doubt from the present work that the reaction is actually endothermic rather than exothermic as reported by Martell.⁶

The relatively large positive entropy changes shown in Table I are of the same order of magnitude as the values reported for the formation of a

number of other chelates and complex ions,¹³⁻¹⁵ and are probably associated with an increase in the number of particles for the reaction, together with the partial neutralization of charge.

The entropy change accompanying reaction 1 can be represented by

$$\Delta S^0 = S_{MY}^0 - S_Y^0 + xS_{H_2O}^0 - S_M^0 \quad (9)$$

where S^0 is the standard partial molal entropy of the species involved. Of the quantities on the right side of the equation only the partial molal entropy of the metal ion (S_M^0) is known. S_Y^0 , though unknown, is rigidly constant for the series. In Fig. 1 the observed values of ΔS^0 are plotted against ($-S_M^0$) for the corresponding metal ions.⁹ It will be observed that the majority of points fall reasonably close to a straight line of unit slope, as would be expected if the quantity ($S_{MY}^0 - S_Y^0 + xS_{H_2O}^0$) were constant throughout the series. With the exception of the points for copper, zinc and lead, the average deviation from the line is about 2.5 e.u., which, in view of the possible combined errors of ΔF^0 , ΔH^0 and S_M^0 , is probably as good as could be expected. While the quantity ($S_{MY}^0 + xS_{H_2O}^0$) is apparently constant for the systems whose points fall near the line in Fig. 1, it does not necessarily follow that the quantities S_{MY}^0 and $xS_{H_2O}^0$ are *individually* constant throughout the series. This is a consequence of the fact that S_{MY}^0 may be a function of x . There are six potentially reactive groups in the ethylenediaminetetraacetate ion. There seems to be no very conclusive evidence, however, that all six take part in bonding for the metals studied here.¹⁶ Possibly the number of bonding groups may vary from metal to metal. In general, it might be expected that each bonding group of the ethylenediaminetetraacetate ion would displace one water molecule from the coordination sphere of the metal ion. Since $S_{H_2O}^0$ is equal to 16.7 e.u.,¹⁷ each increase of one unit in x would be expected to increase ΔS^0 by this amount, if there were no compensating effect. Each additional group of the ethylenediaminetetraacetate ion bound to the metal ion will, however, in general give rise to an additional metal containing ring. The entropy decrease accompanying ring formation is given by Cobble⁴ as 14 e.u. This value would be expected to vary somewhat from compound to compound but it is evident that the decrease in entropy accompanying the formation of an additional ring nearly compensates for the increase due to the release of one water molecule. It can be seen from this discussion that the agreement as shown in Fig. 1 does not constitute proof of a similarity in structure for these complexes, although such a structural similarity probably does exist for the complexes of at least some of the metals studied.

The greatest deviations in Fig. 1 are shown by the

- (13) H. Freiser, *Record Chem. Progress*, **14**, 199 (1953).
- (14) W. D. Johnston, Ph.D. Thesis, University of Pittsburgh, 1953.
- (15) M. Calvin and N. C. Melchior, *THIS JOURNAL*, **70**, 3270 (1948).
- (16) D. H. Busch and J. C. Bailar, Jr., *ibid.*, **75**, 4574 (1953). These authors have presented evidence that the ethylenediaminetetraacetate ion functions as a hexadentate donor in its Co(III) complex.
- (17) W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, N. Y., 1952.

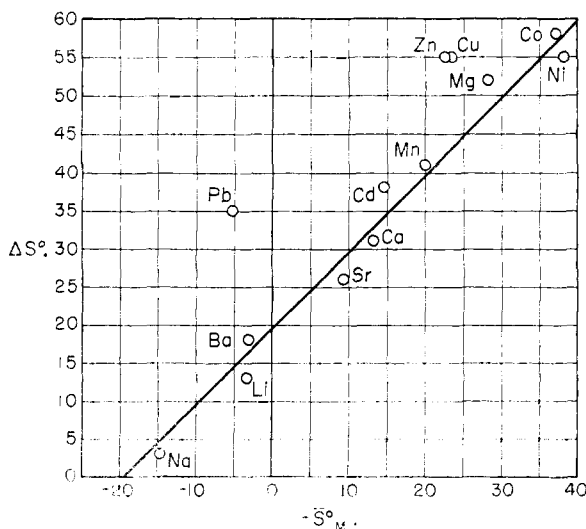


Fig. 1.—Relationship between $-S_M^0$ and ΔS^0 .

points for zinc, copper and lead. These deviations may indicate structural differences of a different type, or may possibly indicate a difference in coordination number for the hydrated cation as opposed to that for the metal ion in the ethylenediaminetetraacetate chelate. It does not appear possible to draw more definite conclusions until additional structural evidence becomes available.

The values of ΔH^0 given in Table I are of interest from several points of view. First, the rather small negative values are not as great numerically as might be expected from the high stabilities of many of these complexes. It is apparent that in many cases it is the high positive value for ΔS^0 that is responsible for much of the stability. This is particularly true for the Mg(II) complex where ΔH^0 is positive. A second point of interest is found in the order of decreasing negative values for ΔH^0 . This order is Pb(II) > Cd(II) > Cu(II) > Ni(II) > Ca(II) > Mn(II) > Ba(II) > Zn(II) > Sr(II) > Co(II) > Na(I) > Li(I) > Mg(II). This order differs considerably from the corresponding order for ΔF^0 : Cu(II) > Ni(II) > Pb(II) > Co(II) > Zn(II) > Cd(II) > Mn(II) > Ca(II) > Mg(II) > Sr(II) > Ba(II) > Li(I) > Na(I). The latter stability order differs only in occasional reversal of adjacent metals from the corresponding relative stability orders which have been found for a number of other chelating agents with the same metals.^{1,14,18-20} There are available, unfortunately, insufficient data to establish definitely whether the order of decreasing values of ΔH^0 normally parallels that of ΔF^0 (or $\log K$) for all the metals studied. For such data as are available, however,^{13,14,21,22} such a parallelism does appear to exist, so that the descending order of $-\Delta H^0$ for the chelates of ethylenediaminetetraacetate may perhaps be "abnormal."

Van Uitert and Fernelius²³ have suggested that chelate bond strength is related to the product ($X_a X_m$) where X_m is the electronegativity of the metal ion in the complex and X_a is the electronegativity of the other bonding atom. The same authors were able to show that in a number of cases a linear relationship exists between $\log K_1$ ²⁴ and X_m for a series of chelates derived from the same chelating agent and metal ions of a given charge type or between ZX_m and $\log K$, when the metal ions are of more than one charge type.^{23,25} These relationships presumably hold only because ΔS^0 for the reactions are, in these cases, small, or sufficiently constant, or else vary in such a way, as to make $\log K_1$ (or ΔF^0) a measure of relative bond strength. In general, a plot of ΔH^0 vs. X_m (or ZX_m) for the same reaction should give better agreement. Insufficient data are available in the literature to adequately test this.

(18) R. Nasanen, *Suomen Kemistilehti*, **B2**, 11 (1953).

(19) L. G. Van Uitert and W. C. Fernelius, *THIS JOURNAL*, **76**, 375 (1954).

(20) W. D. Johnston and H. Freiser, *ibid.*, **74**, 5239 (1952).

(21) W. S. Fyfe, *J. Chem. Soc.*, 2023 (1952).

(22) G. H. McIntyre, Jr., Ph.D. Thesis, Pennsylvania State College, 1953.

(23) L. G. Van Uitert and W. C. Fernelius, *THIS JOURNAL*, **76**, 379 (1954).

(24) K_1 refers to the reaction: $M^{+2} + R^{-n} \rightleftharpoons MR^{+2-n}$.

(25) L. G. Van Uitert and W. C. Fernelius, A.E.C. Report NYO-3372, 1952.

An attempt to plot the ΔH^0 values obtained in the present work vs. ZX_m did not give the expected straight line or, indeed, any simple relationship. It is evident that some additional factor must be involved for the chelates of ethylenediaminetetraacetate. A qualitative inspection of the data makes it seem probable that this factor is ion size. For example, one of the largest cations studied, Pb(II), has the most negative value for ΔH^0 , while the smallest divalent cation studied, Mg(II), has the most positive value. In Fig. 2, ΔH^0 is plotted against the quantity $ZX_m r$, where Z is the charge on the metal cation, X_m is its electronegativity²⁶ and r is the ionic radius of the cation.²⁷ While there is appreciable scatter, a linear relationship appears to exist. Part of the scatter can be attributed to errors in the various quantities involved. The remaining scatter may be associated with structural differences in the various chelates. As discussed above, the number of potentially reactive groups of the ethylenediaminetetraacetate ion actually bound to the metal may not be the same in all cases. It seems apparent that ΔH^0 should be a function of the number of groups bound. It is doubtful that the relationship is a very straightforward one, however, due to complications of changes in bond strain and repulsive forces as more groups are attached to the metal ion. It is also possible that the relationship in Fig. 2 is oversimplified and that the consideration of additional terms might give better agreement.

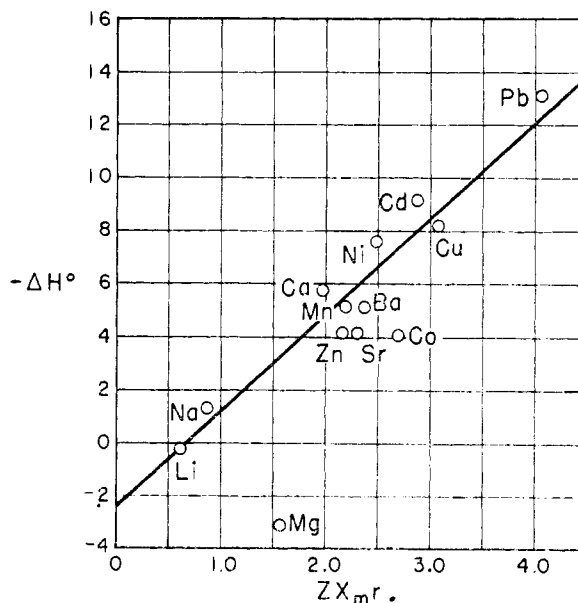


Fig. 2.—Relationship between the quantity $ZX_m r$ and ΔH^0 .

The fact that ΔH^0 for reaction 1 tends to become more negative as r increases suggests that steric hindrance and bond strain become smaller as the metal ion becomes larger. In addition, repulsive forces between the negatively charged bound carboxyl groups should become smaller as r increases.

(26) M. Haissinsky, *J. Phys. Radium*, [8] **7**, 7 (1946); *J. Chem. Phys.*, **15**, 152 (1947).

(27) R. J. P. Williams, *J. Phys. Chem.*, **58**, 121 (1954).

Williams²⁷ 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 sys-

tems, 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.

EAST PITTSBURGH, PA.

[CONTRIBUTION FROM ARTHUR D. LITTLE, INC.]

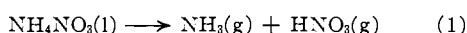
The Dissociation Pressure and Free Energy of Formation of Ammonium Nitrate

BY GEORGE FEICK

RECEIVED JUNE 14, 1954

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



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 Cottrell⁴ 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

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

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

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