rate constants are associated with low activation energies—*ca.* 5000 cal. in iso-dielectric media.

In conclusion, it may be said that the equations of Amis and Cook[18] and Amis and Potts[17] allow reasonably good calculation of the differences of log A in iso-composition and iso-dielectric media, and of the differences of $E_{\text{exp.}}$ in similar media. Also it should be mentioned that while the last term of equation (8) accounts reasonably for the variation in rate with dielectric constant it does not account for the variation with temperature. This situation has been studied in detail by Amis and Jaffe.[19]

Summary

The rate of decomposition of the azodicarbonate ion has been measured, in dilute sodium hydroxide in water and with addition of dioxane up to 60%, at five temperatures from 15 to 35°.

From these rates, molar hydrogen ion catalysis constants at zero ionic strength were calculated. Their variation with dielectric constant was found to agree satisfactorily with the predictions of electrostatic theory.

Temperature coefficients were determined for iso-composition and iso-dielectric solvents and energies and entropies of activation were calculated for comparison with the Eyring "absolute rate" and the collision rate theories. The results, especially in the isodielectric media, show agreement with theory quite comparable to that in other reactions reported in the literature.

Previous interpretation of the nature and mechanism of the reaction is substantiated.

WASHINGTON SQUARE COLLEGE
NEW YORK, N. Y.

RECEIVED JANUARY 14, 1944

---

(18) Amis and Cook, THIS JOURNAL, **63**, 2621 (1941).

(19) Amis and Jaffe, *J. Chem. Phys.*, **10**, 646 (1942).

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR, BERKELEY, CALIFORNIA]

Heats of Formation of Solid and Liquid $Mn(NO_3)_2 \cdot 6H_2O$[1]

BY C. HOWARD SHOMATE[2] AND FRANK E. YOUNG[2]

The heats of fusion of certain nitrates are important factors in thermal calculations pertaining to the nitrogen dioxide[3] process for extracting manganese from low-grade ores, now being studied by the Bureau of Mines. Available values for these nitrates antedate modern thermochemical methods and are of questionable accuracy. This paper presents new determinations of the heats of formation of solid and liquid manganous nitrate hexahydrate and of the heat of fusion of this compound. In a later paper, similar data will be reported for the nitrates of barium, calcium, and magnesium.

Method and Materials

The manganous nitrate hexahydrate used in this work was prepared by Dr. E. H. Huffman by dissolving electrolytic manganese (purity at least 99.9 per cent) in reagent-grade nitric acid. The manganese was added slowly to control the temperature until the acid had been largely used up. Finally, an excess of manganese was contacted until brown oxide of manganese just started to form, indicating virtually complete exhaustion of the acid. After filtration, a small amount of 30% hydrogen peroxide was added to clear up a slight discoloration remaining in the solution. The material then was evacuated with an oil pump and stored over a mixture of potassium hydroxide and calcium chloride. At this stage, the product was solid at room temperature, and analysis showed 4.13 moles of water per mole of manganous nitrate. Melting, with addition of enough water to bring the composition to the hexahydrate, yielded material with a melting point of 24.9°. Two fractional crystallizations produced crystals melting at 25.0°, which was not raised by further fractionation. The latter material constituted the final product. It analyzed 19.15% manganese (theoretical, 19.14%).

Heats of formation and the heat of fusion were determined by measuring the heat of solution of the salt in 1 N sulfuric acid in the apparatus described by Southard.[4] The 1.000 N sulfuric acid was prepared by dilution of reagent grade concentrated sulfuric acid and was standardized against sodium carbonate.

The calorimetric system was calibrated electrically, using a 100-ohm manganin heater. The heater current was measured by the potential drop across a 0.01-ohm standard resistance calibrated by the National Bureau of Standards. The usual heating period during a calibration was 600 seconds, which gave a temperature rise of about 400 μv. (about 0.36°). The temperature readings were estimated to 0.01 μv. from galvanometer deflections. All measurements were made with a White double potentiometer.

The results are expressed in defined calories (1 cal. = 4.1833 int. joules),[5] and all formula weights were calculated from the 1941 International Atomic Weights. All weights were corrected to a vacuum basis, using 1.8 for the density of solid manganous nitrate hexahydrate and 1.7 for the liquid.

Measurements and Results

The average sample weight of manganous nitrate hexahydrate (5.2895 g.) corresponds to the weight of manganese used in determinations of the heat of solution of manganese metal by Southard and Shomate,[6] whose value is adopted here. This sample weight corresponds to a dilution of 1 mole of anhydrous salt in $49.23H_2SO_4 \cdot 5{,}355H_2O$.

The skeleton equations necessary to calculate the heats of formation of solid and liquid man-

---

[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

[2] Chemists, Western Region, Bureau of Mines.

[3] Dean, Fox and Back, Bureau of Mines, Rept. of Investigations 3626, 30 pp. (1942).

[4] Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

[5] Mueller and Rossini, *Am. J. Physics*, **12**, 1 (1944).

[6] Southard and Shomate, THIS JOURNAL, **64**, 1770 (1942).

ganous nitrate hexahydrate and its heat of fusion are given in Tables I, II and III. The uncertainties given in the last column of each table are twice the standard deviations of the means of the experimental results involved. This method of calculating uncertainties was discussed by Rossini and Deming[7] and was adopted by Shomate[8] in a previous paper on the thermochemistry of manganese compounds. In the tables, the resulting values of the heats of formation and the corresponding uncertainties have been rounded to the nearest 10 calories.

Heat of Formation of $Mn(NO_3)_2 \cdot 6H_2O$(l).—A summary of the data needed to calculate the heat of formation of liquid manganese nitrate hexahydrate is given in Table I.

TABLE I

HEAT OF FORMATION OF $Mn(NO_3)_2 \cdot 6H_2O$(l) (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
(1) $Mn + 2H^+ \longrightarrow Mn^{++} + H_2$	−54,406	50
(2) $H_2 + N_2 + 3O_2 \longrightarrow 2H^+ + 2NO_3^-$	−97,853	305
(3) $Mn(NO_3)_2 \cdot 6H_2O(l) \longrightarrow Mn^{++} + 2NO_3^- + 6H_2O(l)$	−5,096	6
(4) $6H_2 + 3O_2 \longrightarrow 6H_2O(l)$	−409,908	60
(5) $Mn + N_2 + 6O_2 + 6H_2 \longrightarrow Mn(NO_3)_2 \cdot 6H_2O(l)$	−557,070	310

$$\Delta H_5 = \Delta H_1 + \Delta H_2 - \Delta H_3 + \Delta H_4$$

The heat of reaction (1) in 1.000 *N* sulfuric acid was obtained from the value of Southard and Shomate[6] by applying a small correction to change from their acid strength, 1.006 *N*, to the present strength, 1.000 *N*. This correction was estimated from the data of Grau and Roth[9] as 50 ± 10 cal. per mole to give $\Delta H_{298.16} = -54,406$ from Southard and Shomate's value of $\Delta H_{298.16} = -54,356$ for 1.006 *N* acid.

Reaction (2) represents the heat of formation of nitric acid in $MnSO_4 \cdot 48.23H_2SO_4 \cdot 5,355H_2O$. The heat of this reaction was obtained by considering the following series of reactions

$$(6) \quad H_2 + N_2 + 3O_2 + 26.50H_2O \longrightarrow 2HNO_3 \cdot 26.50H_2O$$

$$(7) \quad 2HNO_3 \cdot 26.50H_2O + MnSO_4 \cdot 48.23H_2SO_4 \cdot 5,355H_2O \longrightarrow Mn(NO_3)_2 \cdot 49.22H_2SO_4 \cdot 5,381.5H_2O$$

$$(8) \quad Mn(NO_3)_2 \cdot 49.23H_2SO_4 \cdot 5,355H_2O + 26.50H_2O \longrightarrow Mn(NO_3)_2 \cdot 49.23H_2SO_4 \cdot 5,381.5H_2O$$

The desired heat of formation is $\Delta H_2 = \Delta H_6 + \Delta H_7 - \Delta H_8$. The heat of reaction (6) is obtainable from the work of Becker and Roth,[10] who reported $\Delta H_{293.1} = -14,855$ for the reaction, $Aq + 1/2N_2 + 5/4O_2 + 1/2H_2O(l) = HNO_3(0.05M)$. Forsythe and Giauque[11] have corrected this value to 25°, making $\Delta H_{298.16} = -15,075$. Employing Rossini's[12] heat of formation of liquid water, there is obtained $\Delta H_{298.16} = -49,234 \pm 151$ as the heat of formation of $HNO_3(0.05M)$ from the elements. The correction to the degree of dilution of reaction (6) may be made from the data of Becker and Roth,[13] +37 ± 4 cal., to yield finally $\Delta H_{298.16} = 2(-49,197 \pm 152) = -98,394 \pm 304$ cal. for the heat of reaction (6).

The heats of reactions (7) and (8) were directly determined in the present work as 460 ± 21 and −81 ± 10 calories, respectively, thus yielding $\Delta H_{298.16} = -97,853 \pm 305$ for reaction 2.

Six determinations of ΔH_3 were made, the results being −5098, −5091, −5101, −5085, −5102, and −5085, with a mean of −5096 ± 6 calories, after applying a correction of +18 ± 2 calories for the directly determined heat of dilution of the solution by the water of hydration. The average final temperature of the solution experiments was 25.5°. Data are not available for making the minor correction to 25.0°. It was necessary to carry out the solution experiments at slightly above 25° to avoid freezing any of the liquid manganous nitrate hexahydrate before solution.

The heat of formation obtained by subtracting ΔH_3 from the sum of ΔH_1, ΔH_2, and ΔH_4 is −557,070 ± 310 calories per mole.

Heat of Fusion of Manganous Nitrate Hexahydrate.—The heat of fusion was determined from the heats of solution of the solid and liquid as shown in Table II.

TABLE II

HEAT OF FUSION OF $Mn(NO_3)_2 \cdot 6H_2O$

Reaction	ΔH, room temp.	Uncertainty
(9) $Mn(NO_3)_2 \cdot 6H_2O(c) \longrightarrow Mn^{++} + 2NO_3^- + 6H_2O$	+4,510	11
(10) $Mn(N_3)O_2 \cdot 6H_2O(l) \longrightarrow Mn^{++} + 2NO_3^- + 6H_2O$	−5,096	6
(11) $Mn(NO_3)_2 \cdot 6H_2O(c) \longrightarrow Mn(NO_3)_2 \cdot 6H_2O(l)$	+9,610	10

$$\Delta H_{11} = \Delta H_9 - \Delta H_{10}$$

The heat of solution (9) was determined in the same way as the heat of solution of the liquid (10), previously discussed as reaction (3). The value +4510 ± 11 for ΔH_9 is the mean of five results: +4499, +4500, +4520, +4504, and +4524. The correction for dilution by the water of hydration (+18 calories) is included. Because of glass formation when the liquid nitrate was frozen in ice, it was necessary to freeze each sample in a sealed glass bulb in carbon dioxide–ethyl alcohol mixture and allow it to warm slowly to about 21° before putting it into the calorimeter. It was found best to measure the heat of solution of the solid at a mean final temperature of 21.9°. Unfortunately, no data are available to permit accurate correction to 25°. For this reason, the calculated uncertainty, 10

---

(7) Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(8) Shomate, THIS JOURNAL, **65**, 785 (1943).

(9) Grau and Roth, *Z. anorg. Chem.*, **188**, 195 (1930).

(10) Becker and Roth, *Z. Elektrochem.*, **40**, 842 (1934).

(11) Forsythe and Giauque, THIS JOURNAL, **64**, 48 (1942).

(12) Rossini, *Bur. Standards J. Research*, **22**, 407 (1939).

(13) Becker and Roth, *Z. physik. Chem.*, **A174**, 104 (1935).

calories, may be somewhat smaller than the true uncertainty in the heat of fusion.

Heat of Formation of Solid Manganous Nitrate Hexahydrate.—The heat of formation of the solid salt may be found by adding the heat of formation of the liquid and the heat of solidification. The skeleton equations for this calculation are shown in Table III.

TABLE III

HEAT OF FORMATION OF $Mn(NO_3)_2 \cdot 6H_2O(c)$

Reaction	$\Delta H_{298.16}$	Uncertainty
(12) $Mn + N_2 + 6O_2 + 6H_2 \longrightarrow$ $Mn(N_3O)_2 \cdot 6H_2O(l)$	−557,070	310
(13) $Mn(NO_3)_2 \cdot 6H_2O(c) \longrightarrow$ $Mn(NO_3)_2 \cdot 6H_2O(l)$	+9,610	10
(14) $Mn + N_2 + 6O_2 + 6H_2 \longrightarrow$ $Mn(NO_3)_2 \cdot 6H_2O(c)$	−566,680	310

$$\Delta H_{14} = \Delta H_{12} - \Delta H_{13}$$

Reactions (12) and (13) were discussed above as reactions (5) and (11), respectively. The value of the heat of formation of solid manganous nitrate, −566,680 ± 310 calories, is subject to the same lack of correction to 25° as the heat of fusion discussed under equation (9). By comparison with the uncertainty of 310 calories, however, this correction probably is not significant.

Discussion.—The results of this investigation are summarized in Table IV. In the reactions involving liquid water, Rossini's[12] value of the heat of formation of water is used.

The previous values for the reactions in Table IV, as summarized in the compilation of Bichowsky and Rossini,[14] are not in good agreement with the present results and emphasize the necessity of being critical of the older heat of formation data of nitrates. They tabulate −564.2 kilocalories for the heat of formation of solid manganous nitrate hexahydrate based upon Thomsen's data for the heat of formation of manganous hydroxide, the heat of solution of manganous nitrate hexahydrate in water, for which Thomsen reported +6.15 kilocalories, and the heat of reaction of manganous hydroxide with nitric acid. Combining the above value for the solid with the heat of fusion, 8.26 kilocalories, from the data of Riesenfeld and Milchsack,[15] Bichowsky and Rossini give −555.9 kilocalories for the heat of formation of the liquid nitrate from the elements. These older data, except for the heat of fusion, are reported at 291.16°K.

TABLE IV

HEATS OF REACTION (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
$Mn + N_2 + 6O_2 + 6H_2 \longrightarrow$ $Mn(NO_3)_2 \cdot 6H_2O(l)$	−557,070	310
$Mn + N_2 + 6O_2 + 6H_2(l) \longrightarrow$ $Mn(NO_3)_2 \cdot 6H_2O(c)$	−566,680	310
$Mn + N_2 + 3O_2 + 6H_2O(l) \longrightarrow$ $Mn(NO_3)_2 \cdot 6H_2O(l)$	−147,160	310
$Mn + N_2 + 3O_2 + 6H_2O(l) \longrightarrow$ $Mn(NO_3)_2 \cdot 6H_2O(c)$	−156,770	310
$Mn(NO_3)_2 \cdot 6H_2O(c) \longrightarrow$ $Mn(NO_3)_2 \cdot 6H_2O(l)$	+9,610	10

Summary

The heats of formation from the elements of liquid and solid manganous nitrate hexahydrate and the heat of fusion of this compound have been determined at room temperature by measuring the heats of solution in 1 *N* sulfuric acid. The results are, respectively, $\Delta H_{298.16} = -557,070 \pm 310$, $-566,680 \pm 310$, and $+9,610 \pm 10$ calories per mole.

BERKELEY, CALIF. RECEIVED FEBRUARY 7, 1944

---

[14] Bichowsky and Rossini, Thermochemistry of the Chemical Substances, Reinhold Publishing Corporation, New York, N. Y., 1936.

[15] Riesenfeld and Milchsack, *Z. anorg. allgem. Chem.*, **85**, 401 (1914).

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR, BERKELEY, CALIFORNIA]

Heats of Formation of $Mg(NO_3)_2$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$ and $Ba(NO_3)_2$[1]

BY FRANK E. YOUNG[2]

Thermal calculations pertaining to the nitrogen dioxide cyclic process for the hydrometallurgical extraction of manganese from ores require accurate values of the heats of formation of the nitrates of several constituents, particularly manganese, barium, calcium, and magnesium. No value of the heat of formation of anhydrous magnesium nitrate is available, and the existing heats of formation of the other nitrates are based largely on older data of uncertain reliability. New values of the heats of formation of solid and liquid manganous nitrate hexahydrate were reported in a previous paper.[3] The present paper records new determinations of the heats of formation of anhydrous magnesium, calcium, and barium nitrates, magnesium nitrate hexahydrate and calcium nitrate tetrahydrate.

---

[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. (Not copyrighted.)

[2] Chemist, Western Region, Bureau of Mines.

[3] Shomate and Young, THIS JOURNAL, **66**, 771 (1944).