The value for manganese dioxide is 1.2 units lower than that given by Millar.[4a] Part of this difference is the result of his less certain extrapolation from about 72°K. (because of the effect of the specific heat "hump"), and the remainder is attributable to the previously discussed defects in his data. The manganese carbide value fortuitously is nearly identical with a previously assumed quantity, 23.7.[12]

Related Thermal Data

A redetermination of the heat of formation of manganese dioxide, nearing completion in this Laboratory, probably will enable the calculation of a more precise free energy value than is possible at present. Bichowsky and Rossini[13] adopt −123,000 calories per mole as the heat of formation of this substance. The entropy of the dioxide and the entropies of the elements[14] involved lead to $\Delta S_{298.16} = -43.9$. Combination of these values yields $\Delta F^0_{298.16} = -109{,}900$ calories per mole as the free energy of formation of manganese dioxide from the elements.

Bichowsky and Rossini give −23,000 calories per mole as the heat of formation of manganese carbide. The same value also has been listed by Roth.[15] From the entropies there is obtained $\Delta S_{298.16} = -0.6$. The free energy of formation from the elements, therefore, is $\Delta F^0_{298.16} = -22{,}800$ calories per mole. The error in this result may be taken as of the same order of magnitude as is attributed to the heat of formation, namely, ±2000 calories.

Summary

The specific heats of manganese carbide and manganese dioxide have been measured in the temperature range 51 to 298°K.

Manganese dioxide has a marked anomaly in its specific heat curve with the peak at 92.12 ± 0.05°K. The total heat absorbed between 85 and 100°K. was measured as 102.5 calories per mole.

The following entropy values were computed—$S_{298.16} = 23.6 \pm 0.3$ calories per mole per degree for manganese carbide and $S_{298.16} = 12.7 \pm 0.1$ for manganese dioxide.

The calculated free energies of formation from the elements are $\Delta F^0_{298.16} = -22{,}800$ calories per mole and $\Delta F^0_{298.16} = -109{,}900$ calories per mole, respectively, for the carbide and dioxide.

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(12) Kelley, Bureau of Mines Bulletin 407, 1935, 66 pp.

(13) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

(14) Kelley, Bureau of Mines Bulletin 434, 1941, 115 pp.

(15) Roth, *Z. angew. Chem.*, **42**, 981 (1929).

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[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Manganomanganic Oxide and Manganese Dioxide[1]

BY C. HOWARD SHOMATE[2]

The determination of the heats of formation of substances of metallurgical importance is one of the fields of study of the Pacific Experiment Station of the Bureau of Mines. In a previous paper[3] measurements of the heats of formation of manganous oxide and manganous sulfate were reported. The present paper presents similar data for manganomanganic oxide and manganese dioxide.

Previous values of the heats of formation of manganomanganic oxide and manganese dioxide depend almost entirely upon combustion experiments.[4] Combustion of manganese metal or of its oxides always produces a mixture of oxides and large errors in the heats of formation so obtained may result from rather minor errors in the analysis of the resulting mixture. In addition, most of the combustion reactions require a promotor such as charcoal or paraffin oil and in some instances the heat evolved in burning the promoter has been several times the magnitude of the heat of reaction under investigation. It is not surprising, therefore, that values in the literature for the heat of formation of manganomanganic oxide vary from −318,000 to −345,000 cal. per mole and for manganese dioxide from −119,600 to −126,000 cal. per mole. In view of these wide variations it appeared desirable to redetermine these quantities

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

(2) Assistant chemist, Western Region, Bureau of Mines.

(3) Southard and Shomate, THIS JOURNAL, **64**, 1770 (1942).

(4) (a) Le Chatelier, *Compt. rend.*, **122**, 80 (1896); (b) Mixter, *Am. J. Sci.*, [4] **30**, 193 (1910); (c) Ruff and Gersten, *Ber.*, **46**, 394 (1913); (d) Roth and Müller, *Z. angew. Chem.*, **42**, 981 (1929); (e) Simon and Fehér, *Z. Elektrochem.*, **38**, 137 (1932); (f) Siemonsen, *ibid.*, **45**, 637 (1939).

by entirely different methods. The general method used in the present investigation involves the measurement of heats of solution of manganese metal and the oxides in solutions of reducing agents. From the results of such measurements and known related data, the heats of formation of manganomanganic oxide and manganese dioxide may be obtained.

Method and Materials

The heat of formation of manganomanganic oxide was determined by two distinct methods, *viz.:* first, from the heats of solution of manganese metal and the oxide in 1 *N* sulfuric acid solution containing potassium iodide and second, from the heats of solution of the metal, the oxide, and hydrogen peroxide in sulfuric acid solution (approx. 2 *N*) containing a high concentration of ferrous ammonium sulfate.

Two methods also were employed for manganese dioxide, comprising, first, the heats of solution of manganese metal, manganese dioxide and hydrogen peroxide in the sulfuric acid solution containing ferrous ammonium sulfate, and, second, the heats of solution of manganese dioxide, manganous oxide and manganomanganic oxide in the same sulfuric acid–ferrous ammonium sulfate solution. It was not possible to use the sulfuric acid–potassium iodide method in this instance as the rate of solution of manganese dioxide in this medium was found to be too slow for accurate heat-of-solution determinations.

All measurements of heats of solution were made using the previously described[5] apparatus. The defined calorie (1 cal. = 4.1833 int. joules) was used throughout. All weights were corrected to vacuum and formula weights all are in accordance with the 1941 International Atomic Weights.

The manganese metal was an electrolytic product at least 99.9% pure. It was degassed by heating to 850° in vacuum (10^{-5} mm.) and slowly cooled to room temperature. For the measurements in 1 *N* sulfuric acid–potassium iodide solutions, the metal was crushed before degassing to pass a 20-mesh and be retained on a 60-mesh screen. This particle size gave a reaction time of twenty minutes in the 1 *N* sulfuric acid–potassium iodide solutions but reacted much too violently in the 2 *N* sulfuric acid–ferrous ammonium sulfate solution. In the latter instance larger particles of about 0.1 g. mass were used, a reaction time of forty to sixty minutes being obtained.

The manganese dioxide was the material used previously by Kelley and Moore.[6] It was prepared by dissolving pure electrolytic manganese in reagent quality concentrated nitric acid, followed by evaporation and slow decomposition at 200° for several days. This process gave a product that was steel-gray in color and unusually dense. The material was pulverized and heated at 500° in a stream of pure oxygen until removal of water was complete, oxygen being used to prevent decomposition. The final product was analyzed by reduction with hydrogen to manganous oxide and by reaction with excess sodium oxalate followed by back-titration with permanganate. The reduction method gave for the ratio MnO/"MnO_2" 81.50% and 81.48% (calcd. 81.59%), while the sodium oxalate method gave for the ratio O*/"MnO_2" 18.40%, 18.47%, and 18.46% (calcd. 18.41%). The reaction time in the 2 *N* sulfuric acid–ferrous ammonium sulfate solution varied from twenty to one hundred and sixty minutes depending upon circumstances.

Manganomanganic oxide was prepared by decomposing in vacuum at about 1050° a sample of manganese dioxide obtained by electrolysis of manganous sulfate in 20% sulfuric acid. Analysis by reaction with excess ferrous ammonium sulfate followed by back-titration with dichromate solution gave 7.00, 7.00 and 7.01% available oxygen (calcd. 6.99%). By hydrogen reduction to manganous oxide the ratio MnO/"Mn_3O_4" was obtained as 93.06% and 93.03% (calcd. 93.01%). In 1 *N* sulfuric acid–potassium iodide solution the reaction time of this material was forty to fifty minutes, while in 2 *N* sulfuric acid–ferrous ammonium sulfate solution the reaction time was only twenty minutes.

The manganous oxide originally was prepared by Millar[7] by reduction of higher oxides with hydrogen at 1100°. It was further purified by Southard and Shomate,[8] who removed most of the silica which had been introduced by flaking of Millar's reaction vessel, by flotation in tetrabromoethane followed by drying in high vacuum at 250°. Analysis then showed less than 0.04% silica and 77.42%, 77.45% manganese (calcd. 77.44%).

The hydrogen peroxide solution was a Merck product of high purity ("Superoxol"). Analysis by titration with permanganate gave 24.96% hydrogen peroxide before the measurements and 24.78% hydrogen peroxide after the measurements, two months later. The reaction between the hydrogen peroxide and the 2 *N* sulfuric acid–ferrous ammonium sulfate solution was nearly complete in less than one minute as indicated by heat evolution, but the last part of the reaction was very slow, two to five hours being required to reach final equilibrium.

Measurements and Results

Each of the heats of formation is the result of a series of reactions, the skeleton equations for which are given in Tables I to IV. The uncertainties given in the last columns are in most instances twice the standard deviations of the means of the several experimental values obtained. These errors, therefore, represent precision of the values and do not include unknown or unaccounted for systematic errors,[9] which, however, are assumed to be small compared with the former. The probability that the true value lies within the range defined by twice the standard deviation of the mean is about 0.95. To establish the uncertainty of a result which is the sum of two or more other values, the square root of the sum

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(5) Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

(6) Kelley and Moore, THIS JOURNAL, **65**, 782 (1943).

(7) Millar, *ibid.*, **50**, 1875 (1928).

(8) Southard and Shomate, *ibid.*, **64**, 1770 (1942).

(9) (a) Rossini, *Chem. Rev.*, **18**, 252 (1936); (b) Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

of the squares of the individual uncertainties is taken.

For a few reactions in Tables I to IV heat values were taken from the literature and in some instances the assignments of uncertainties are only rough estimates. Such estimates probably are on the conservative side (*i. e.*, the magnitudes of the ascribed uncertainties are too great).

Heat of Formation of Manganomanganic Oxide. Method 1.—Table I gives the summary of results employed in obtaining the heat of formation of manganomanganic oxide by the sulfuric acid–potassium iodide method.

TABLE I

HEAT OF FORMATION OF Mn_3O_4 (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$, cal.	Uncertainty, cal.
(1) $3Mn + 6H^+ \rightarrow 3Mn^{++} + 3H_2$	−162,774	142
(2) $I_2 + I^- \rightarrow I_3^-$	1,136	16
(3) $Mn_3O_4 + 8H^+ + 31^- \rightarrow$ $3Mn^{++} + I_3^- + 4H_2O$	− 78,243	62
(4) $4H_2 + 2O_2 \rightarrow 4H_2O$	−273,272	40
(5) $H_2 + I_2 \rightarrow 2H^+ + 2I^-$	− 25,021	200
(6) $3Mn + 2O_2 \rightarrow Mn_3O_4$	−331,650	260

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

The complete equation for reaction (1) is as follows: $3Mn + 115.71H_2SO_4 \cdot 54HI \cdot 30K_2SO_4 \cdot 15{,}803H_2O(soln.) \longrightarrow 3MnSO_4 \cdot 112.71H_2SO_4 \cdot 54HI \cdot 30K_2SO_4 \cdot 15{,}803H_2O(soln.) + 3H_2(g)$. The initial solution was prepared by dissolving appropriate amounts of potassium iodide, potassium sulfate and water in sulfuric acid solution. Three determinations of the heat of reaction (1) were made, the results being −53,926, −53,903 and −53,962 cal. per mole of manganese, respectively. The mean is −53,930 cal. with a standard deviation of 17 calories. It is necessary to correct this result for the vaporization of water by the evolved hydrogen. It was assumed that no hydrogen remained in the solution by the time equilibrium was reached and that it was saturated with water vapor on leaving the solution. Taking the partial pressure of water over the solution as 23.0 mm. at 25° and the heat of vaporization of water as 10,500 cal. per mole at 25°, the correction becomes 328 cal. per mole of evolved hydrogen. Thus the true value for reaction (1) as written is 3 × (−53,930 − 328) or −162,774 cal. Allowing an error of 10% in the correction, the resultant uncertainty in ΔH_1 is $3\sqrt{34^2 + 33^2} = 142$ cal.

Equation (2) represents the reaction occurring when solid iodine is dissolved in the solution in which manganese metal previously had been dissolved. Three determinations of ΔH_2 gave 1151, 1122, and 1136 cal., respectively. The mean is 1136 cal. and the standard deviation is 8 cal.

Equation (3) represents the dissolution of manganomanganic oxide in a solution such that the final composition is identical with that resulting after reactions (1) and (2). Four determinations of ΔH_3 were made, yielding −78,171, −78,210, −77,303 and −78,287 cal., respectively. The mean is −78,243 cal. with a standard deviation of 31 cal. These figures have been corrected for the heat of dilution by the water formed in reaction (3). This was determined by a separate experiment to be only 10 cal., heat being evolved by the dilution.

The heat of formation of liquid water was determined by Rossini[10] as $\Delta H_{298.16} = -68{,}318$ cal. per mole, with an uncertainty of 10 calories. Therefore, ΔH_4 is $-273{,}272 \pm 40$ cal.

Equation (5) represents the formation of 2 moles of hydriodic acid in a solution of composition, $115.71H_2SO_4 \cdot 54HI \cdot 30K_2SO_4 \cdot 15{,}803H_2O$. To obtain the corresponding heat, first, 10% hydriodic acid solution ($2HI \cdot 128H_2O$) was dissolved in $115.71H_2SO_4 \cdot 54HI \cdot 30K_2SO_4 \cdot 15{,}675H_2O$. The reaction was endothermic, 431 cal. being absorbed. Second, water corresponding to H_2O was dissolved in the same solution, 294 cal. being evolved. Finally, these results were combined with the value for the reaction

$$H_2 + I_2 + 128H_2O \longrightarrow 2HI \cdot 128H_2O;\ \Delta H_7 = -25{,}746 \quad (7)$$

ΔH_7 was obtained by recalculation of data given by Bichowsky and Rossini.[11] These authors give −26,480 cal. for reaction (7) based upon 5910 cal. per mole as the heat of formation of gaseous hydrogen iodide. However, for the latter quantity Roth[12] and co-workers give 6240, Günther and Wekua,[13] 6266 (correction made to constant pressure), and Murphy,[14] 6325. The mean of these latter values is adopted here, 6277 cal. per mole, thus making $\Delta H_7 = -25{,}746$ cal. Therefore, ΔH_5 becomes −25,746 + 431 + 294 or −25,021 cal.

The summation, $\Delta H_6 = \Delta H_1 + \Delta H_2 - \Delta H_3 + \Delta H_4 - \Delta H_5$, gives $\Delta H_6 = -331{,}650 \pm 260$ cal. per mole as the heat of formation of manganomanganic oxide by method 1.

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

(11) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

(12) Roth, Boerger and Siemonsen, *Atti X° congr. intern. chim.*, **2**, 775 (1938).

(13) Günther and Wekua, *Z. physik. Chem.*, **154A**, 193 (1931).

(14) Murphy, *J. Chem. Phys.*, **4**, 344 (1936).

Heat of Formation of Manganomanganic Oxide. Method 2.—The thermal values obtained to yield the heat of formation of manganomanganic oxide by the sulfuric acid–ferrous ammonium sulfate method are summarized in Table II.

TABLE II

HEAT OF FORMATION OF Mn_3O_4 (CAL. PER MOLE)

	Reaction	$\Delta H_{298.16}$, cal.	Uncertainty. cal.
(8)	$3Mn + 6H^+ \rightarrow 3Mn^{++} + 3H_2$	−172,128	573
(9)	$Mn_3O_4 + 2Fe^{++} + 8H^+ \rightarrow 3Mn^{++} + 2Fe^{+++} + 4H_2O$	− 86,135	40
(10)	$H_2O_2\cdot 5.7H_2O + 2Fe^{++} + 2H^+ \rightarrow 2Fe^{+++} + 7.7H_2O$	− 63,375	106
(11)	$H_2 + O_2 + 5.7H_2O \rightarrow H_2O_2\cdot 5.7H_2O$	− 45,640	200
(12)	$2H_2 + O_2 \rightarrow 2H_2O$	−136,636	20
(13)	$3Mn + 2O_2 \rightarrow Mn_3O_4$	−331,640	620

$\Delta H_{13} = \Delta H_8 - \Delta H_9 + \Delta H_{10} + \Delta H_{11} + \Delta H_{12}$

Manganese, manganomanganic oxide and hydrogen peroxide ($H_2O_2\cdot 5.7H_2O$) in amounts represented in equations (8), (9) and (10) each were dissolved in a solution corresponding to 202.77 $H_2SO_4\cdot 106.20Fe(NH_4)_2(SO_4)_2 9915H_2O$.

Four determinations were made for reaction (8), the results being −57,319, −56,869, −57,004, and −57,071 cal. per mole of manganese. The mean is −57,066 cal. with a standard deviation of 94 cal. Correction for the vaporization of water by the evolved hydrogen was computed as discussed above, 21.7 mm. being taken as the vapor pressure in the present instance. This correction is 310 cal. per mole of hydrogen. The result for reaction (8) is, therefore, 3 × (−57,066 − 310) or −172,128 cal. with an uncertainty of 573 cal.

Three determinations of ΔH_9 were made, −86,150, −86,096 and −86,159 cal. The mean is −86,135 ± 20 cal. These results have been corrected by 75 cal. which represents the heat of dilution by the water formed in reaction (9) as determined by a separate experiment.

Seven determinations of ΔH_{10} were made, −63,344, −63,514, −63,369, −63,298, −63,124, −63,457 and −63,519. The mean is −63,375 ± 53 cal. As mentioned earlier, although the bulk of the heat in reaction (10) was evolved in a short time interval, the final attainment of equilibrium was very slow, which resulted in more uncertain heat interchange corrections. This accounts for the variations in the above results. Here again correction is necessary for dilution by water. This was determined by separate experiment to be 144 cal., and is included in the above results.

The heat of reaction (11) has been taken from Bichowsky and Rossini's[11] compilation and, as before, Rossini's[10] value of the heat of formation of water is employed for reaction (12).

Summing the results in Table II, $\Delta H_8 - \Delta H_9 + \Delta H_{10} + \Delta H_{11} + \Delta H_{12}$, yields ΔH_{13} or −331,640 ± 620 cal. as the heat of formation of manganomanganic oxide by method 2.

Heat of Formation of Manganese Dioxide. Method 1.—Table III gives a summary of the results measured for the various steps involved in obtaining the heat of formation of manganese dioxide by the sulfuric acid–ferrous ammonium sulfate method involving hydrogen peroxide.

TABLE III

HEAT OF FORMATION OF MnO_2 (CAL. PER MOLE)

	Reaction	$\Delta H_{298.16}$, cal.	Uncertainty, cal.
(14)	$Mn + 2H^+ \rightarrow Mn^{++} + H_2$	− 57,376	191
(15)	$MnO_2 + 2Fe^{++} + 4H^+ \rightarrow Mn^{++} + 2Fe^{+++} + 2H_2O$	− 42,089	86
(16)	$H_2O_2\cdot 5.7H_2O + 2Fe^{++} + 2H^+ \rightarrow 2Fe^{+++} + 7.7H_2O$	− 63,375	106
(17)	$H_2 + O_2 + 5.7H_2O \rightarrow H_2O_2\cdot 5.7H_2O$	− 45,640	200
(18)	$Mn + O_2 \rightarrow MnO_2$	−124,300	310

$\Delta H_{18} = \Delta H_{14} - \Delta H_{15} + \Delta H_{16} + \Delta H_{17}$

Manganese, manganese dioxide and hydrogen peroxide ($H_2O_2\cdot 5.7H_2O$) in amounts represented by equations (14), (15), and (16) were each dissolved in a solution of composition $67.59H_2SO_4\cdot 35.40Fe(NH_4)_2(SO_4)_2\cdot 3305H_2O$.

The heat of reaction (14) was discussed previously as the heat of reaction (8). Reaction (16) is the same as reaction (10) except for a difference in concentration. Determinations made at proper concentrations for each of reactions (10) and (16) and at intermediate concentrations gave no appreciable differences or noticeable trend. A correction of 144 calories was applied to the heat of reaction (16) for the heat evolved in the dilution by the water formed in the reaction. Reaction (17) also is identical with reaction (11).

Three determinations of the heat of reaction (15) were made. The results are −42,082, −42,167 and −42,018 cal., the mean being −42,089 ± 43 cal. Each value has been corrected by 37 cal. to account for the heat evolved in the dilution by the water formed in the reaction. This correction was determined experimentally.

Summing the results as $\Delta H_{14} - \Delta H_{15} + \Delta H_{16} + \Delta H_{17}$ leads to $\Delta H_{18} = -124,300 \pm 310$ cal. for the heat of formation of manganese dioxide by method 1.

Heat of Formation of Manganese Dioxide, Method 2.—The second method employed for manganese dioxide is similar to the first in that it involves heat-of-solution measurements in sulfuric acid–ferrous ammonium sulfate solutions. It differs from the first in that the use of hydrogen peroxide is eliminated. This is accomplished by employing manganomanganic oxide and manganous oxide as indicated in Table IV where the results for method 2 are summarized.

TABLE IV

HEAT OF FORMATION OF MnO_2 (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$, cal.	Uncertainty. cal.
(19) $Mn_3O_4 + 2Fe^{++} + 8H^+ \rightarrow 3Mn^{++} + 2Fe^{+++} + 4H_2O$	− 86,210	40
(20) $2MnO + MnO_2 + 2Fe^{++} + 8H^+ \rightarrow 3Mn^{++} + 2Fe^{+++} + 4H_2O$	−108,919	42
(21) $3Mn + 2O_2 \rightarrow Mn_3O_4$	−331,650	250
(22) $2Mn + O_2 \rightarrow 2MnO$	−184,080	48
(23) $Mn + O_2 \rightarrow MnO_2$	−124,860	260

$$\Delta H_{23} = \Delta H_{19} - \Delta H_{20} + \Delta H_{21} - \Delta H_{22}$$

Reactions (19) and (20) were carried out by dissolving equivalent amounts of manganomanganic oxide and a mixture of manganous oxide and manganese dioxide ($2MnO + MnO_2$) in a solution containing $202.77H_2SO_4 \cdot 106.20Fe(NH_4)_2(SO_4)_2 \cdot 9915H_2O$. The heat of reaction (19) is the same as that of reaction (9) except that in this instance no heat of dilution correction is necessary because it is balanced by an identical effect in reaction (20). Five separate determinations of the heat of reaction (20) were made. The results are −108,878, −108,971, −108,951, −108,864 and −108,931, the mean being −108,919 ± 21 cal. Three of these results were obtained by dissolving manganous oxide and manganese dioxide simultaneously and two by dissolving the materials consecutively. The latter was done to correct the former for slight deviations in weight in making up the mixtures.

The heat of reaction (21) is, of course, the value obtained from the measurements discussed earlier in this paper while that of reaction (22) has been reported previously by Southard and Shomate,[3] except that the ascribed uncertainty was made to conform to the basis of calculation adopted in the present paper.

The combination of quantities, $\Delta H_{19} - \Delta H_{20} + \Delta H_{21} - \Delta H_{22}$, results in ΔH_{23} or −124,860 ± 260 cal. as the heat of formation of manganese dioxide by method 2.

Discussion

The very close agreement of the two results obtained for the heat of formation of manganomanganic oxide is, of course, entirely fortuitous as is evident from the ascribed uncertainties. The value to be adopted from the present work is $\Delta H_{298.16} = -331{,}650 \pm 250$ cal./mole. Table V summarizes the available values for this substance. It is seen that the present value falls between the results of the combustion experiments of Ruff and Gersten and of Roth and Siemonsen. The present methods are believed to yield more accurate values than any of the combustion work in spite of the more elaborate scheme of reactions involved. At least it is evident that even the more recent combustion work has not yielded an incontrovertible value.

TABLE V

SUMMARIZED HEAT OF FORMATION VALUES OF Mn_3O_4 (CAL. PER MOLE)

Investigator	Year	Method	ΔH (formation)
LeChatelier[4a]	1896	Combustion	−328,000
Ruff and Gersten[4c]	1913	Combustion	−329,000
Roth and Müller[4d]	1929	Combustion	−345,000
Siemonsen[4f]	1939	Combustion	−336,500
Shomate	1942	Solution	−331,650

The weighted mean of the results for the heat of formation of manganese dioxide from the present work is $\Delta H_{298.16} = -124{,}640 \pm 200$ cal./mole. This value is compared with other available figures in Table VI.

TABLE VI

SUMMARIZED HEAT OF FORMATION VALUES OF MnO_2 (CAL. PER MOLE)

Investigator	Year	Method	ΔH (formation)
LeChatelier[4a]	1896	Bomb, with charcoal	−125,200
Mixter[4b]	1910	Bomb, with S and Na_2O_2	−119,600
Simon and Fehér[4e]	1932	Dissociation pressure	−120,600
Siemonsen[4f]	1939	Bomb, with oil	−125,400
Shomate	1942	Solution	−124,640

Again the present result is considered more reliable than those from bomb calorimeter experiments. However, the disagreement with the most recently result, that of Siemonsen, is not too bad considering the probable uncertainties in both measurements.

Summary

The heat of formation of manganomanganic oxide was obtained by two solution methods involving the use of, first, sulfuric acid–potassium iodide solutions and second, sulfuric acid–ferrous ammonium sulfate solutions. The results of the two methods agree, the mean value being $\Delta H_{298.16} = -331{,}650 \pm 250$ cal. per mole.

The heat of formation of manganese dioxide was obtained by two solution methods involving the use of sulfuric acid–ferrous ammonium sulfate solutions, both with and without the use of hydrogen peroxide. Agreeing results were obtained, the weighted mean of which is $\Delta H_{298.16} = -124{,}640 \pm 200$ cal. per mole.

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[CONTRIBUTION NO. 471 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Dilution and Relative Heat Contents of Aqueous Solutions of Lanthanum Chloride and Lanthanum Sulfate at 25°

BY C. C. NATHAN,[1] W. E. WALLACE[2] AND A. L. ROBINSON

The heat of dilution of dilute solutions of electrolytes has been the subject of many investigations in recent years.[3] Extrapolation of such measurements to infinite dilution and comparison of the limiting slopes so obtained with the predictions of the Debye–Hückel theory[4,5] has been a matter of considerable interest. Earlier studies did not include electrolytes of higher valence type than 2–2. In this paper are presented measurements on lanthanum chloride and sulfate. From these data relative apparent and relative partial molal heat contents have been calculated. All measurements were made at 25 ± 0.02°. With the chloride the range of concentrations extended from 0.1 to 0.00006 molal, while with the sulfate the range was 0.025 to 0.000015 molal.

Materials.—The sulfate and chloride were prepared from a supply of lanthanum oxide procured from the Eastman Kodak Co. The analysis indicated a product of high purity containing less than 0.01% of other rare earths and heavy metals.

Lanthanum chloride was prepared by dissolving the oxide in hydrochloric acid and precipitating the highly soluble salt by saturation with dry hydrogen chloride gas at 0°. The hydrated product was freed of water and excess hydrogen chloride by heating at 230° in a stream of dry hydrogen chloride gas. Heating the chloride directly in the presence of air results in the loss of hydrogen chloride, as well as water, and the formation of basic chlorides.[6] Determinations of the lanthanum and chloride content of the anhydrous salt indicated its purity to be 99.7% or better.

Lanthanum sulfate was prepared from the hydrated lanthanum chloride by repeated digestion with sulfuric acid until all the hydrogen chloride had been driven off. The excess sulfuric acid was removed by heating the sample in an electric furnace maintained at 650°. This temperature is somewhat critical since at lower temperatures the lanthanum acid sulfates are not completely converted to the normal sulfate, while at higher temperatures the normal sulfate itself is decomposed into oxides of lanthanum and sulfur.[7] The anhydrous lanthanum sulfate was then dissolved in seven times its weight of ice-water, the salt being added in small portions to the water while agitating with a mechanical stirrer. The small amount of residue was filtered from the solution, and the filtrate slowly warmed to 35° while stirring continuously. The enneahydrate, $La_2(SO_4)_3 \cdot 9H_2O$, crystallized[8] from the solution between 30 and 35°. The crystals were washed with water, then with acetone and dried at 50° until free of the odor of acetone. Determinations of the lanthanum, sulfate and water contents of the salt indicated a purity equal to or greater than 99.6%.

Procedure.—The dilutions were carried out in the apparatus and manner described by Wallace and Robinson.[9] The only significant change in apparatus was the replacement of the old pipets of gilded brass with new ones of monel metal. The volumes of the new pipets were 10.351 and 10.389 ± 0.005 ml., and the amounts of water in the two sides of the calorimeter were respectively chosen as 1000 and 1003 ± 1 ml. in order to give equal dilution ratios on both sides of the calorimeter. This ratio was 96.6.

The most concentrated solutions of sulfate and chloride were prepared directly by dissolving a weighed sample in a known volume of water. Other solutions were made by volumetric dilutions of the strongest. The concentrations were expressed on a weight basis with the aid of density data determined at 25 ± 0.2°. Equations relating density to molarity are

$$d^{25} = 0.9971 + 0.227\,c \text{ for } LaCl_3 \text{ below 0.1 molar} \tag{1}$$

$$d^{25} = 0.9971 + 0.584\,c \text{ for } La_2(SO_4)_3 \text{ below 0.025 molar} \tag{2}$$

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[2] Research Fellow in Chemistry under a grant made by the Carnegie Institution of Washington and the Buhl Foundation of Pittsburgh.

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