

unit higher than that given by Aston, Szasz and Fink<sup>2</sup> and 0.36 entropy unit lower than that given by Parks, Huffman and Thomas.<sup>3</sup>

Moore, Renquist and Parks<sup>9</sup> and Spitzer and Huffman<sup>10</sup> have recently made careful determinations of the heat of combustion of cyclohexane. The mean of these two values which are in excellent agreement is  $\Delta H_R = -936.33$  kcal./mole at 298.16° K. This datum in conjunction with the entropy reported in this paper have been utilized

TABLE VI

THE MOLAL FREE ENERGY OF FORMATION OF LIQUID CYCLOHEXANE AT 298.16° K.

Heat of comb., $\Delta H^0$ , kcal.	$\Delta H^0_f$ , kcal.	$\Delta S$ , cal./degree	$\Delta F^0_f$ , kcal.
-936.33	-37.75	-146.71	5.99

(9) Moore, Renquist and Parks, *THIS JOURNAL*, **62**, 1505 (1940).

(10) Unpublished results.

to calculate the free energy of formation of liquid cyclohexane. The data are summarized in Table VI.

In conclusion we wish to thank the Shell Development Company for preparing the cyclohexane and for financial assistance which made possible this investigation.

### Summary

The heat capacity, heat of transition and heat of fusion of cyclohexane have been measured.

A description of the apparatus and experimental method, including a new method of heat transfer by mechanical contact, has been presented.

The molal entropy and free energy of liquid cyclohexane at 298.16° K. have been calculated,  $S = 48.84$  cal./degree,  $\Delta F^0_f = 5.99$  kcal.

BARTLESVILLE, OKLAHOMA RECEIVED MARCH 15, 1943

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

## Heats of Formation of MgO, MgCl<sub>2</sub>, MgCl<sub>2</sub>·H<sub>2</sub>O, MgCl<sub>2</sub>·2H<sub>2</sub>O, MgCl<sub>2</sub>·4H<sub>2</sub>O, and MgCl<sub>2</sub>·6H<sub>2</sub>O<sup>1</sup>

BY C. HOWARD SHOMATE<sup>2</sup> AND EUGENE H. HUFFMAN<sup>3</sup>

The determination of heats of formation of substances of technological importance is one of the programs of study of the Pacific Experiment Station of the Bureau of Mines. Previous papers<sup>4</sup> have dealt with the heats of formation of several manganese and calcium compounds.

The present paper reports heat-of-formation values of MgO, MgCl<sub>2</sub>, MgCl<sub>2</sub>·H<sub>2</sub>O, MgCl<sub>2</sub>·2H<sub>2</sub>O, MgCl<sub>2</sub>·4H<sub>2</sub>O and MgCl<sub>2</sub>·6H<sub>2</sub>O. All of these substances had been studied previously, but the data are rather obsolete and could not be considered trustworthy for many purposes. To remedy this situation the present work was undertaken.

### Materials

The magnesium metal was supplied by the Bureau of Mines Laboratory at Pullman, Wash. It was made by carbon reduction of magnesium oxide, followed by vacuum sublimation. The total impurities were stated to be less than 0.01%, excepting surface oxidation. The material used in the measurements was taken from the interior of a

large ingot and was exposed only during the time required for weighing and sealing in glass bulbs.

Magnesium oxide was made by igniting magnesium hydroxide prepared from reagent-quality magnesium chloride and ammonium hydroxide. Care was taken in washing the hydroxide free of chlorides, and the ignition was carried out in a silica flask for one hundred hours during which time the temperature was raised gradually from 400 to 1000°. Analysis showed 60.36% Mg (calcd. 60.32%) and 99.90% MgO by titration.

The anhydrous magnesium chloride employed had been prepared previously by Kelley and Moore.<sup>5</sup> It was re-treated before use by heating in a silica flask at 600° in a stream of dry hydrogen chloride to remove any water that had been taken up during removal from Kelley and Moore's apparatus and subsequent storage. Analysis showed 74.27% Cl (calcd. 74.46%), 25.65% Mg (calcd. 25.54%), and 0.15% MgO.

Magnesium chloride monohydrate was prepared by heating equimolal quantities of anhydrous magnesium chloride and magnesium chloride dihydrate *in vacuo* at 135° for sixteen hours. Analysis gave 62.44% Cl (calcd. 62.62%), 21.57% Mg (calcd. 21.47%), and 0.14% MgO.

Magnesium chloride dihydrate was prepared from reagent quality magnesium chloride hexahydrate. The latter was heated in air at 103° until approximately 2 moles of water were removed. It was then heated in a stream of dry hydrogen chloride, the temperature being raised over a period of thirty hours from 170 to 220°. This treatment

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

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(4) (a) Southard, *Ind. Eng. Chem.*, **32**, 442 (1940); (b) Kelley, Southard, and Anderson, Bureau of Mines Technical Paper 625, 1941; (c) Southard and Shomate, *THIS JOURNAL*, **64**, 1770 (1942); (d) Shomate, *ibid.*, **65**, 785 (1943).

(5) Kelley and Moore, *THIS JOURNAL*, **65**, 1264 (1943).

gave a product having a little less water than that corresponding to the dihydrate. The calculated additional water needed was added by diffusion, and the material was reheated in a sealed, evacuated flask at 103° for seven hours to distribute the water evenly. Analysis gave 54.04% Cl (calcd. 54.03%), 18.61% Mg (calcd. 18.53%), and 0.01% MgO.

Magnesium chloride tetrahydrate was prepared from *c. p.* magnesium oxide and hydrochloric acid. The crystals were filtered by suction and heated at 103° until constant weight was obtained (one hundred hours). Analysis gave 42.29% Cl (calcd. 42.39%), 14.63% Mg (calcd. 14.54%), and 0.02% MgO.

The magnesium chloride hexahydrate was prepared by storing reagent-grade material containing some excess water over 80% sulfuric acid for seven days. The product contained 34.90% Cl (calcd. 34.88%), 12.02% Mg (calcd. 11.96%), and no MgO.

### Method

The heats of formation were determined by dissolving the compounds and magnesium metal in 1 *N* hydrochloric acid and measuring the resulting heat effects. The apparatus used was described in some detail by Southard.<sup>4a</sup> The energy equivalent of the calorimetric system was determined electrically, employing a 100-ohm manganin heater, and determining the current by measuring the potential drop across a 0.01-ohm standard resistance, calibrated by the National Bureau of Standards. Time was measured with a stop watch calibrated by comparison with a standard chronometer of the Astronomy Department of the University of California. All measurements were made with a White 10,000  $\mu$ V. double potentiometer.

The defined calorie (1 cal. = 4.1833 int. joules) is used throughout, and all formula weights are in accord with the 1941 International Atomic Weights. All weights were corrected to vacuum, using the following densities: magnesium oxide, 3.4; anhydrous magnesium chloride, 2.32; magnesium chloride monohydrate, 2.2; magnesium chloride dihydrate, 2.1; magnesium chloride tetrahydrate, 1.8; and magnesium chloride hexahydrate, 1.56.

### Measurements and Results

Each of the heats of formation is the resultant of a series of reactions, the skeleton equations for which are given in Tables I to VI. The equations for dissolution of the magnesium metal and compounds are for reactions in 1 *N* hydrochloric acid at a dilution of 1 mole of reacting substance in 77.2HCl·4,190H<sub>2</sub>O. The actual weights of these substances employed are equivalent

to the average weight of the metal samples, 0.5725 g.

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, which, however, are assumed to be small in comparison with the random variations in a series of results. 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 of the squares of the individual uncertainties is taken. These methods of ascribing uncertainties in thermochemical experiments are described more fully by Rossini and Deming.<sup>6</sup> It will be noted that the resultant value in each table and its uncertainty have been rounded to the nearest 10 calories.

**Heat of Formation of MgO.**—Table I summarizes the data for obtaining the heat of formation of magnesium oxide.

TABLE I  
HEAT OF FORMATION OF MgO (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
(1) $\text{Mg} + 2\text{H}^+ \longrightarrow \text{Mg}^{++} + \text{H}_2$	-111,322	41
(2) $\text{MgO} + 2\text{H}^+ \longrightarrow \text{Mg}^{++} + \text{H}_2\text{O}$	-35,799	21
(3) $\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}$	-68,318	10
(4) $\text{Mg} + \frac{1}{2}\text{O}_2 \longrightarrow \text{MgO}$	-143,840	50

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

Six determinations of the heat of reaction (1) were made, the results being -110,985, -111,007, -111,039, -110,981, -111,012 and -110,949 cal. per mole of magnesium, respectively. The mean is -110,996 cal. with an uncertainty of 25 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 water vapor pressure over the solution as 22.9 mm. at 25° and the heat of vaporization of water as 10,500 cal. per mole, the correction is 326 cal. per mole of evolved hydrogen. The vapor pressure of hydrogen chloride gas over 1 *N* hydrochloric acid

<sup>6</sup> Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

is so small that the correction for the heat involved in removal of hydrogen chloride gas from the solution by the evolved hydrogen is entirely negligible. Thus the true value for reaction (1) as written is  $-110,996-326$  or  $-111,322$  cal. Allowing an error of 10% in the water-vaporization correction, the resultant uncertainty in  $\Delta H_1$  is  $\sqrt{25^2 + 33^2} = 41$  cal.

Five determinations of  $\Delta H_2$  were made, obtaining  $-35,775$ ,  $-35,821$ ,  $-35,783$ ,  $-35,826$  and  $-35,791$  cal. per mole, respectively. The mean is  $-35,799$  cal., with an uncertainty of 21 calories. Each of these determinations was corrected for the heat of dilution by the water formed in reaction (2). This was determined by separate experiment to be only 5 calories, heat being evolved in the dilution.

The heat of formation of liquid water, reaction (3), was determined by Rossini<sup>7</sup> as  $\Delta H_{298.16} = -68,318$  cal. per mole, with an uncertainty of 10 calories. The summation,  $\Delta H_1 - \Delta H_2 + \Delta H_3$ , gives  $\Delta H_4 = -143,840 \pm 50$  cal. per mole as the heat of formation of magnesium oxide.

**Heat of Formation of  $\text{MgCl}_2$  (anhydrous).**—Table II summarizes the heats-of-solution measurements involved in determining the heat of formation of anhydrous magnesium chloride.

TABLE II  
HEAT OF FORMATION OF  $\text{MgCl}_2$  (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
(5) $\text{Mg} + 2\text{H}^+ \rightarrow \text{Mg}^{++} + \text{H}_2$	-111,322	41
(6) $\text{MgCl}_2 \rightarrow \text{Mg}^{++} + 2\text{Cl}^-$	-36,566	18
(7) $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{H}^+ + 2\text{Cl}^-$	-78,460	100
(8) $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$	-153,220	110
$\Delta H_8 = \Delta H_5 - \Delta H_6 + \Delta H_7$		

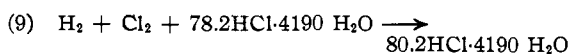
The heat of reaction (5) was discussed previously as the heat of reaction (1).

Seven determinations of the heat of reaction (6) were made. The results are  $-36,532$ ,  $-36,578$ ,  $-36,596$ ,  $-36,571$ ,  $-36,536$ ,  $-36,567$ , and  $-36,583$  cal., the mean being  $-36,566$  cal. with an uncertainty of 18 cal. These results were corrected for the heat evolved in the dissolution of the 0.15% magnesium oxide present in the samples; this correction amounted to 74 calories.

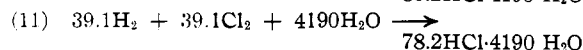
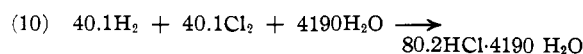
The complete equation for reaction (7) is as follows:  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) + \text{MgCl}_2 \cdot 75.2\text{HCl} \cdot 4190 \text{H}_2\text{O} (\text{soln.}) \rightarrow \text{MgCl}_2 \cdot 77.2\text{HCl} \cdot 4190 \text{H}_2\text{O} (\text{soln.})$ . It was assumed that the heat of this reaction is the same as that of the following reaction, since

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

the ionic strengths of the respective solutions are equal.



The heat of reaction (9) can be found as the difference in the heats of the following reactions



The data of Rossini<sup>8</sup> on the heat of formation of hydrochloric acid and the accurate determinations of the heats of dilution of hydrochloric acid made by Sturtevant<sup>9</sup> were used in determining  $\Delta H_9$  as  $-78,460$  cal. An uncertainty of 100 calories has been assigned to this value.

Summing the results in Table II,  $\Delta H_5 - \Delta H_6 + \Delta H_7$  yields  $\Delta H_8 = -153,220 \pm 110$  cal. as the heat of formation of anhydrous magnesium chloride.

**Heat of Formation of  $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ .**—The results of the measurements for the evaluation of the heat of formation of magnesium chloride monohydrate are summarized in Table III.

TABLE III  
HEAT OF FORMATION OF  $\text{MgCl}_2 \cdot \text{H}_2\text{O}$  (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
(12) $\text{Mg} + 2\text{H}^+ \rightarrow \text{Mg}^{++} + \text{H}_2$	-111,322	41
(13) $\text{MgCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Mg}^{++} + 2\text{Cl}^- + \text{H}_2\text{O}$	-27,132	20
(14) $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{H}^+ + 2\text{Cl}^-$	-78,460	100
(15) $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	-68,318	10
(16) $\text{Mg} + \text{Cl}_2 + \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O}$	-230,970	110
$\Delta H_{16} = \Delta H_{12} - \Delta H_{13} + \Delta H_{14} + \Delta H_{15}$		

Reactions (12), (14) and (15) are identical with reactions (1), (7) and (3), respectively, which have been discussed above.

Six determinations of the heat of reaction (13) were made, obtaining  $-27,123$ ,  $-27,155$ ,  $-27,141$ ,  $-27,095$ ,  $-27,160$  and  $-27,117$  cal. per mole, respectively. Each of these results has been corrected by 5 calories, the amount of heat evolved in the dilution by the water formed in reaction (13). A correction of 103 calories was also made for the 0.14% MgO impurity.

$\Delta H_{12} - \Delta H_{13} + \Delta H_{14} + \Delta H_{15}$  gives  $\Delta H_{16} = -230,970$  cal. per mole for the heat of formation of  $\text{MgCl}_2 \cdot \text{H}_2\text{O}$  from the elements, with an uncertainty of 110 calories.

(8) Rossini, *ibid.*, **9**, 679 (1932).

(9) Sturtevant, *THIS JOURNAL*, **62**, 584 and 3265 (1940).

**Heat of Formation of  $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ .**—In Table IV are summarized the various thermal values used for the determination of the heat of formation of magnesium chloride dihydrate.

TABLE IV

HEAT OF FORMATION OF $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ (CAL. PER MOLE)		
Reaction	$\Delta H_{28,16}$	Uncertainty
(17) $\text{Mg} + 2\text{H}^+ \longrightarrow \text{Mg}^{++} + \text{H}_2$	-111,322	41
(18) $\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \longrightarrow \text{Mg}^{++} + 2\text{Cl}^- + 2\text{H}_2\text{O}$	-20,613	16
(19) $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{H}^+ + 2\text{Cl}^-$	-78,460	100
(20) $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$	-136,636	19
(21) $\text{Mg} + \text{Cl}_2 + 2\text{H}_2 + \text{O}_2 \longrightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$	-305,810	110
$\Delta H_{21} = \Delta H_{17} - \Delta H_{18} + \Delta H_{19} + \Delta H_{20}$		

The heats of reactions (17) and (19) were discussed as the heats of reactions (1) and (7), respectively.

Seven determinations of  $\Delta H_{18}$  were made, obtaining -20,616, -20,592, -20,618, -20,627, -20,579, -20,642, -20,619 cal. per mole, respectively. The mean is -20,613 cal. per mole, with an uncertainty of 16 cal. Each of these values has been corrected for the heat evolved in the dilution by the water formed in reaction (18). This was determined by separate experiment to be 11 cal. Correction was also made for the heat evolved by the 0.01% magnesium oxide impurity present in the samples: this correction was 10 cal.

Equation (20) is identical with equation (3) except that two moles of water are involved rather than one.

Summing the quantities,  $\Delta H_{17} - \Delta H_{18} + \Delta H_{19} + \Delta H_{20}$  gives for the heat of formation of  $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$  from the elements  $-305,810 \pm 110$  cal. per mole.

**Heat of Formation of  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ .**—The thermal values obtained to evaluate the heat of formation of magnesium chloride tetrahydrate are summarized in Table V.

TABLE V

HEAT OF FORMATION OF $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ (CAL. PER MOLE)		
Reaction	$\Delta H_{28,16}$	Uncertainty
(22) $\text{Mg} + 2\text{H}^+ \longrightarrow \text{Mg}^{++} + \text{H}_2$	-111,322	41
(23) $\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \longrightarrow \text{Mg}^{++} + 2\text{Cl}^- + 4\text{H}_2\text{O}$	-9,230	5
(24) $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{H}^+ + 2\text{Cl}^-$	-78,460	100
(25) $4\text{H}_2 + 2\text{O}_2 \longrightarrow 4\text{H}_2\text{O}$	-273,272	38
(26) $\text{Mg} + \text{Cl}_2 + 4\text{H}_2 + 2\text{O}_2 \longrightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O}$	-453,820	110
$\Delta H_{26} = \Delta H_{22} - \Delta H_{23} + \Delta H_{24} + \Delta H_{25}$		

$\Delta H_{22}$  and  $\Delta H_{24}$  are the same as  $\Delta H_1$  and  $\Delta H_7$ , previously discussed.  $\Delta H_{25}$  is four times Rossini's value for the heat of formation of a mole of liquid water.

Five determinations of the heat of reaction (23) were made, yielding -9220, -9235, -9229, -9233 and -9231 cal. per mole. The mean is -9230 cal. per mole with an uncertainty of 5 calories. Each determination of  $\Delta H_{23}$  was corrected by 22 calories, this amount representing the heat evolved in the dilution by the water formed in the reaction. Each result was also corrected for the heat evolved by the 0.02% magnesium oxide present in the samples; this correction was 28 calories.

The heat of formation of magnesium chloride tetrahydrate from its elements is found as the sum of  $\Delta H_{22} - \Delta H_{23} + \Delta H_{24} + \Delta H_{25}$  or -453,820 cal. per mole, with an uncertainty of 110 cal.

**Heat of Formation of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .**—The various thermal values necessary for the determination of the heat of formation of magnesium chloride hexahydrate are summarized in Table VI.

TABLE VI

HEAT OF FORMATION OF $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (CAL. PER MOLE)		
Reaction	$\Delta H_{28,16}$	Uncertainty
(27) $\text{Mg} + 2\text{H}^+ \longrightarrow \text{Mg}^{++} + \text{H}_2$	-111,322	41
(28) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \longrightarrow \text{Mg}^{++} + 2\text{Cl}^- + 6\text{H}_2\text{O}$	-2,449	3
(29) $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{H}^+ + 2\text{Cl}^-$	-78,460	100
(30) $6\text{H}_2 + 3\text{O}_2 \longrightarrow 6\text{H}_2\text{O}$	-409,908	58
(31) $\text{Mg} + \text{Cl}_2 + 6\text{H}_2 + 3\text{O}_2 \longrightarrow \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	-597,240	120
$\Delta H_{31} = \Delta H_{27} - \Delta H_{28} + \Delta H_{29} + \Delta H_{30}$		

The heats of reactions (27), (29) and (30) have been discussed above. Seven determinations of the heat of reaction (28) were made, obtaining -2444, -2448, -2450, -2453, -2455, -2449 and -2444 cal. per mole, respectively, with a mean of -2449 cal. per mole and an uncertainty of 3 cal. Since  $\Delta H_{28}$  is small compared with other heat-of-solution measurements, dilution effects caused by variations in sample sizes were noticeable. Consequently a correction was applied to each determination to adjust the result to the desired sample size. The average correction was 7 cal. Each determination was also corrected by 33 calories, the amount of heat evolved in the dilution by the water formed in reaction (28). Summing,  $\Delta H_{27} - \Delta H_{28} + \Delta H_{29} + \Delta H_{30}$ , gives  $\Delta H_{31} = -597,240 \pm 120$  cal. per mole as the heat of formation of magnesium chloride hexahydrate.

### Discussion

The heats of formation of the six substances are summarized in Table VII. In column (a) are the heats of formation from the elements, in column (b) the heats of formation from magnesium, chlorine gas, and liquid water, and in column (c) the heats of formation from anhydrous magnesium chloride and liquid water.

TABLE VII  
HEATS OF FORMATION (CAL. PER MOLE)

	$\Delta H_{298.15}^{\circ}$		
	(a) From elements	(b) From Mg, Cl <sub>2</sub> and H <sub>2</sub> O	(c) From MgCl <sub>2</sub> and H <sub>2</sub> O
MgO	-143,840		
MgCl <sub>2</sub>	-153,220	-153,220	0
MgCl <sub>2</sub> ·H <sub>2</sub> O	-230,970	-162,650	-9,430
MgCl <sub>2</sub> ·2H <sub>2</sub> O	-305,810	-169,170	-15,950
MgCl <sub>2</sub> ·4H <sub>2</sub> O	-453,820	-180,550	-27,330
MgCl <sub>2</sub> ·6H <sub>2</sub> O	-597,240	-187,330	-34,110

The present value for the heat of formation of magnesium oxide compares favorably with the combustion value of von Wartenberg,<sup>10</sup> -143,900 cal. per mole, and with the value Kelley and Anderson<sup>11</sup> computed from heat-of-formation and heat-of-decomposition data of magnesium carbonate, -144,090 cal. per mole. It differs considerably, however, from the value of Moose and Parr,<sup>12</sup> -145,800 cal. per mole. The latter obtained their result by direct combustion of magnesium, but as our oxide had been heated to 1000° there is little reason to believe that the difference

(10) von Wartenberg, *Z. Elektrochem.*, **15**, 869 (1909).

(11) Kelley and Anderson, *Bureau of Mines Bulletin* **384**, 1935, p. 26.

(12) Moose and Parr, *This Journal*, **46**, 2656 (1924).

in heat of formation is attributable to difference in physical form of the oxide. The work of Marignac and Berthelot leads to values in the range -143,400 to -145,300 cal. per mole, depending on the method of calculation.<sup>13</sup>

Bichowsky and Rossini<sup>14</sup> list the following heats of formation from the elements of the magnesium chlorides at 291°K.: -153,300 cal. per mole for MgCl<sub>2</sub>, -305,500 for MgCl<sub>2</sub>·2H<sub>2</sub>O, -452,600 for MgCl<sub>2</sub>·4H<sub>2</sub>O and -596,400 for MgCl<sub>2</sub>·6H<sub>2</sub>O. These values are based largely on heat-of-solution measurements of Thomsen. The agreement between these values and our own is better than would have been expected *a priori*. The greatest difference occurs in the case of the tetrahydrate. This difference is about 0.3% of the heat of formation from the elements or 4.5% of that from magnesium chloride and liquid water, the latter being the more significant.

### Summary

The heats of formation of magnesium oxide, anhydrous magnesium chloride, magnesium chloride monohydrate, magnesium chloride dihydrate, magnesium chloride tetrahydrate, and magnesium chloride hexahydrate have been determined by measuring the heats of solution of these materials and magnesium metal in 1 *N* hydrochloric acid.

(13) (a) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, Vol. 2, 1923, p. 1519; (b) *ibid.*, 1st Supplement, 1927, p. 825.

(14) Bichowsky and Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF SOUTHERN CALIFORNIA]

## The Behavior of Trimethylamine, Trimethylammino-sulfur Trioxide and Trimethylamine Oxide toward Sulfur Dioxide

BY ANTON B. BURG<sup>1</sup>

The rapid development of theories explaining the chemical bond, from a mathematical-physical viewpoint, demands a parallel development of purely chemical facts having a fairly simple relation to the new ideas. As a step toward meeting this evident need, it seems appropriate to make comparative studies of complex compounds

(1) The essential results here given were presented at the Detroit meeting of the American Chemical Society, September, 1940. The author wishes gratefully to acknowledge the contribution of Marshall S. Smoler, whose Master's dissertation (University of Chicago Libraries, 1939) describes the preparation and preliminary study of the compound (CH<sub>3</sub>)<sub>3</sub>NSO<sub>2</sub>.

involving the simpler elements. The present paper describes the behavior of trimethylamine, trimethylammino-sulfur trioxide, and trimethylamine oxide toward sulfur dioxide. These relatively simple compounds were selected because they involve no mobile hydrogen atoms, and form a series suitable for comparisons.

Sulfur dioxide reacts with trimethylamine to form a solid addition product, according to the equation

