

### Summary

1. It has been shown that the presence of magnesium ions to the extent of two moles per liter does not affect the potential of the glass electrode.

2. The water error of the glass electrode in magnesium sulfate solutions has been found to conform well with the equation  $\Delta E = SRT/F \ln$

$a'/\text{H}_2\text{O}$  as derived by Dole.

3. It has been shown that the glass electrode is suitable for measuring the "salt error" of the quinhydrone electrode in solutions buffered with only traces of hydrochloric acid, and that this error depends upon the  $p\text{H}$  of the solution.

LEXINGTON, KY.

RECEIVED NOVEMBER 25, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## The Entropy of Water from the Third Law of Thermodynamics. The Dissociation Pressure and Calorimetric Heat of the Reaction $\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}$ . The Heat Capacities of $\text{Mg}(\text{OH})_2$ and $\text{MgO}$ from 20 to 300°K.

BY W. F. GIAUQUE AND R. C. ARCHIBALD

The thermodynamic properties of water are sufficiently important and interesting to invite the fullest possible investigation. The present work was undertaken because it had been shown<sup>1</sup> that the experimental  $\int_0^T C_p d \ln T$  for water does not give the correct entropy. This quantity is accurately known from the band spectrum data.

It seemed desirable to perform at least one experiment in which the third law of thermodynamics would give the entropy of water accurately and in a straightforward manner. The reaction  $\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}$  was selected for this purpose for several reasons. First, a measurable dissociation occurs at a rather low temperature, although not at as low a temperature as we were led to expect from the erroneous available data. Second, the identity of the water molecule should be very completely lost in magnesium hydroxide and such difficulties as are present in ice, or conceivably in water of crystallization, should not be present. Third, the reaction is one which is well adapted to an accurate calorimetric investigation of the heat of reaction. Fourth, the atoms in the substances concerned are all of low atomic weight, which makes the measured and extrapolated quantities of entropy low, with a corresponding increase in the accuracy of the entropy of water derived from the experimental data.

The entropy of water was obtained from the thermodynamic relation

$$S_T(\text{H}_2\text{O}) = S_T(\text{Mg}(\text{OH})_2) - S_T(\text{MgO}) + (\Delta H_T/T) + R \ln P_T \quad (1)$$

where  $\Delta H_T$  and  $P_T$  are the heat and pressure of

(1) Giauque and Ashley, *Phys. Rev.*, **48**, 81 (1933).

dissociation, respectively, at temperature  $T$ . It safely may be assumed that the fugacity is equal to the pressure at the low pressures and high temperatures of the experiment. We may state at once that complete agreement was found between the entropy value obtained as above and that derived from the molecular spectrum of water.

Since this research was undertaken the heat capacity of ice has been reinvestigated accurately by Giauque and Stout.<sup>2</sup> They have shown that the entropy discrepancy is in very exact agreement with the quantitative predictions of Pauling,<sup>3</sup> who bases his calculation on false equilibrium at low temperatures with respect to the random orientation of hydrogen bonds in ice.

More recently Long and Kemp<sup>4</sup> have made similar measurements on deuterium oxide. They have shown that a similar discrepancy exists in this case and find that it also is in quantitative agreement with the calculated discrepancy of Pauling.<sup>3</sup>

While there is no reason to doubt the reliability of the entropy of water as deduced from the accurately known band spectrum, and although this value is strongly supported by the above investigations, we believe that it is very desirable to have one or more third law checks on this important quantity.

**Preparation and Purity of Magnesium Hydroxide and Magnesium Oxide.**—Crystalline magnesium hydroxide was prepared by the method of de Shulten.<sup>5</sup> A wide-mouthed platinum bottle of one liter capacity was used. This fitted closely inside a well-insulated vertical tubular

(2) Giauque and Stout, *THIS JOURNAL*, **58**, 1144 (1936).

(3) Pauling, *ibid.*, **57**, 2680 (1935).

(4) Long and Kemp, *ibid.*, **58**, 1829 (1936).

(5) De Shulten, *Compt. rend.*, **101**, 72 (1885).

electric oven. A typical charge for the bottle was: 1375 g. of potassium hydroxide, 48.5 g. of  $MgCl_2 \cdot 6H_2O$  and 243 cc. of water. The charge was heated in the oven to  $210^\circ C$ . and held at this temperature until the solution became clear. This required about thirty minutes from the time heating was started. It was then allowed to cool to room temperature in the oven. This required about eighteen hours. The solid mass was dissolved out of the platinum bottle with water and filtered through a sintered glass filter. The crystals of magnesium hydroxide remaining on the filter were washed several times with distilled water. When a sufficient quantity of the crystals had been made they were given a final washing with water and dried for two hours in an oven at  $100^\circ C$ .

The crystals were well formed and of an average diameter of about 0.2 mm. A photograph of a representative sample of the crystals is shown in Fig. 1.



Fig. 1.—Photograph of representative sample of magnesium hydroxide crystals. The average diameter was about 0.2 millimeter.

Since the main impurities possible in the magnesium hydroxide are potassium and phosphate from the potassium hydroxide, analyses were made for these substances. These analyses gave potassium as K, 0.15%, and phosphate as  $PO_4$ , less than 0.005% of the magnesium hydroxide. The material was protected carefully from carbon dioxide and a test showed that carbonate was not present.

In order to obtain magnesium oxide as it exists in equilibrium with the magnesium hydroxide used, the hydroxide was decomposed under vacuum at  $300^\circ C$ ., and the temperature raised to  $350^\circ C$ . toward the end of the decomposition. The decomposition was attempted at  $200^\circ C$ . but was very slow. At  $300^\circ$ , however, it was about 95% complete in ten days. All of the measurements on magnesium oxide were made with this material and the results corrected for the amount of magnesium hydroxide present.

The small amount of potassium hydroxide impurity was assumed to have the same heat capacity as magnesium hydroxide. Such error as is involved by this assumption could hardly have an appreciable effect on the heat capacity results. The effect of impurity on the heat of solution measurements will be discussed in that connection.

**The Heat Capacities of Magnesium Hydroxide and Oxide.**—The heat capacities were measured in a manner and calorimeter similar to that described by Giaque and Wiebe,<sup>6</sup> but, the weight of the heavy, hollow, lead-copper, thermally isolated cylinder that served as an enclosure for the calorimeter was about 50% greater. The electrical leads were carried through the protective cylinder by insulated wire sealed in, for a length of about 7 cm., with a low melting alloy.

The calorimeter was of copper 10.8 cm. in length and 3.8 cm. in diameter and with twelve radial vanes. The gold resistance thermometer-heater was wound on the outside of the calorimeter and brought into good thermal contact by Bakelite lacquer. A short German silver tube, through which the calorimeter was filled, was attached to the bottom of the calorimeter. This tube was provided with a soldered cap containing a pin hole through which the air was pumped out and helium admitted, after which the hole was closed with solder. The helium was necessary to ensure good thermal conductivity. The German silver tube permitted soldering without appreciable heating of the calorimeter.

The resistance thermometer was calibrated by means of standard thermocouple No. 16<sup>7</sup> which was attached to the bottom of the calorimeter. A small correction to the original calibration was applied on the basis of a recent comparison with the oxygen and hydrogen vapor pressure thermometers and the melting point,  $54.39^\circ K$ ., and higher transition point,  $43.76^\circ K$ ., of oxygen.

The thermocouple was brought through the protective cylinder in a paraffin filled tube. The resistance thermometer, which gave high precision and accuracy over short intervals of temperature, was calibrated at about five-degree intervals over the entire range of investigation. The calibrating was done concurrently with the heat capacity measurements.

All low temperatures were produced by means of liquid air or liquid hydrogen, transferred from laboratory supply dewars. In calculating energy, 1.0004 absolute joules were taken equal to 1 international joule and 4.185 absolute joules were taken equal to 1 calorie.

The heat capacity data are summarized in Tables I and II and are shown graphically in Figs. 2 and 3. 173.203 g. of magnesium hydroxide and 118.671 g. of magnesium oxide were used in the measurements.

In Table III the data have been presented in the form of values taken from smooth curves through the experimental values. Since the equilibrium measurements had to be extended to higher temperatures than had been indicated by the erroneous available data a considerable extrapolation was necessary in the case of mag-

(6) Giaque and Wiebe, *THIS JOURNAL*, **50**, 101 (1928).

(7) (a) Giaque, Buffington and Schulze, *ibid.*, **49**, 2343 (1927);

(b) Giaque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

TABLE I  
MOLAL HEAT CAPACITY OF MAGNESIUM OXIDE  
Molecular weight 40.32

T, °K.	$\Delta T$ approx.	$C_p$ , cal./deg.	T, °K.	$\Delta T$ approx.	$C_p$ , cal./deg.
20.34	2.9	0.0220	156.19	5.5	4.717
23.05	3.4	.0282	161.39	5.1	4.970
26.08	3.2	.0389	166.76	5.7	5.190
29.16	3.0	.0596	172.75	6.4	5.455
32.07	2.7	.0659	178.83	6.0	5.721
35.17	3.5	.0928	184.81	5.9	5.971
39.15	4.5	.1183	190.51	5.4	6.184
43.40	4.1	.1480	195.81	5.0	6.380
48.30	5.7	.2148	200.72	4.8	6.570
53.52	5.3	.2812	205.76	4.6	6.708
58.26	4.3	.3609	210.20	5.3	6.888
69.01	4.5	.6708	215.36	5.1	7.031
73.62	4.6	.8341	220.34	4.9	7.215
78.46	5.1	1.022	225.06	4.8	7.336
83.53	5.2	1.239	230.50	6.2	7.472
88.77	5.4	1.481	236.51	6.0	7.608
94.26	5.6	1.730	242.55	5.7	7.788
99.94	5.6	1.996	248.29	5.5	7.928
105.51	6.0	2.267	253.74	5.4	8.059
111.23	5.3	2.542	258.99	5.4	8.199
116.04	5.3	2.786	264.18	5.1	8.313
121.57	5.7	3.071	269.15	4.9	8.387
127.56	5.2	3.408	274.10	4.8	8.489
132.60	4.8	3.655	278.78	4.7	8.636
137.25	4.6	3.886	283.90	5.2	8.724
142.03	5.0	4.158	289.19	5.0	8.856
146.78	4.5	4.324	294.25	4.9	9.000
151.39	4.8	4.545	300.68	5.1	9.088

TABLE II  
MOLAL HEAT CAPACITY OF MAGNESIUM HYDROXIDE  
Molecular weight 58.34

T, °K.	$\Delta T$ approx.	$C_p$ , cal./deg.	T, °K.	$\Delta T$ approx.	$C_p$ , cal./deg.
22.07	2.8	0.1143	140.80	6.3	9.036
25.69	2.8	.1889	146.70	5.8	9.489
29.74	4.7	.3142	152.24	5.3	10.02
34.25	4.0	.4665	157.27	4.9	10.36
38.44	3.9	.6145	162.20	5.3	10.73
42.54	4.1	.7871	167.68	5.7	11.18
46.94	3.7	.9973	173.51	5.9	11.68
52.28	6.3	1.292	179.37	5.4	12.14
59.04	7.4	1.678	184.61	5.1	12.50
65.14	5.8	2.094	189.21	4.6	12.88
70.34	4.7	2.489	194.51	6.0	13.24
75.16	4.6	2.869	200.53	5.8	13.66
79.77	4.5	3.268	205.92	5.3	13.98
84.52	4.9	3.713	211.17	5.1	14.35
89.48	5.0	4.168	216.61	5.3	14.59
94.32	4.6	4.609	221.85	5.1	14.92
99.03	4.8	5.085	227.34	5.5	15.23
103.58	4.5	5.498	232.81	5.3	15.56
108.30	5.0	5.931	238.14	5.1	15.86
113.38	5.1	6.452	243.27	4.9	16.08
118.31	4.7	6.950	248.32	4.7	16.38
123.21	5.1	7.411	253.15	4.6	16.61
128.45	5.4	7.953	258.07	5.4	16.82
134.75	5.8	8.470	263.14	5.2	16.97

268.48	5.6	17.20	299.15	5.6	18.52
274.02	5.4	17.52	304.77	5.5	18.62
279.50	5.3	17.79	310.17	5.3	18.81
285.12	5.6	17.99	315.86	5.1	19.01
290.83	5.5	18.14	320.87	5.0	19.15
296.34	5.4	18.35			

nesium hydroxide. The extrapolated values used in the later calculations are included for this reason. A discussion of the probable error introduced by their extrapolation is given later.

The heat capacity of magnesium oxide has been measured at ordinary or higher temperatures by Regnault,<sup>8</sup> Russell,<sup>9</sup> Magnus,<sup>10</sup> McDowell and Howe,<sup>11</sup> Parks and Kelley,<sup>12</sup> and Wilkes.<sup>13</sup>

We have adopted the smoothed values given in the "I. C. T."<sup>14</sup> The curve through these values connects well with the curve through our data below 300°K.

TABLE III  
MOLAL HEAT CAPACITIES OF Mg(OH)<sub>2</sub> AND MgO  
Molecular weights 58.34 and 40.32. Values taken from smooth curves through the data.  $C_p$  in cal./deg. per mole.

T, °K.	MgO, $C_p$	Mg(OH) <sub>2</sub> , $C_p$	T, °K.	MgO, $C_p$	Mg(OH) <sub>2</sub> , $C_p$
20	0.021	0.082	200	6.537	13.62
30	.057	.320	210	6.880	14.24
40	.126	.676	220	7.182	14.83
50	.234	1.158	230	7.460	15.38
60	.397	1.740	240	7.707	15.92
70	.704	2.456	250	7.958	16.44
80	1.084	3.285	260	8.208	16.89
90	1.527	4.213	270	8.440	17.34
100	1.998	5.156	280	8.662	17.76
110	2.482	6.125	290	8.875	18.15
120	3.000	7.090	300	9.070	18.47
130	3.542	8.032	310	(9.20)	18.79
140	4.013	8.93	320	(9.34)	19.12
150	4.476	9.79	350	(9.65)	(19.97)
160	4.905	10.56	400	(10.00)	(21.28)
170	5.330	11.37	450	(10.34)	(22.55)
180	5.760	12.20	500	(10.62)	(23.68)
190	6.173	12.94			

The heat capacity of magnesium oxide has been measured at low temperatures by Günther<sup>15</sup> and by Parks and Kelley.<sup>12</sup> The measurements of Günther are not self-consistent and deviations from the present data range from 70 to 13% low over the interval 40 to 85°K.

(8) Regnault, *Ann. chim. phys.*, **1**, 129 (1841).  
 (9) Russell, *Physik. Z.*, **13**, 59 (1912).  
 (10) Magnus, *ibid.*, **14**, 5 (1913).  
 (11) McDowell and Howe, *J. Am. Ceramic Soc.*, **3**, 185 (1920).  
 (12) Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).  
 (13) Wilkes, *J. Am. Ceramic Soc.*, **15**, 72 (1931).  
 (14) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. V, 1928, p. 99.  
 (15) Günther, *Ann. Physik*, **51**, 828 (1916).

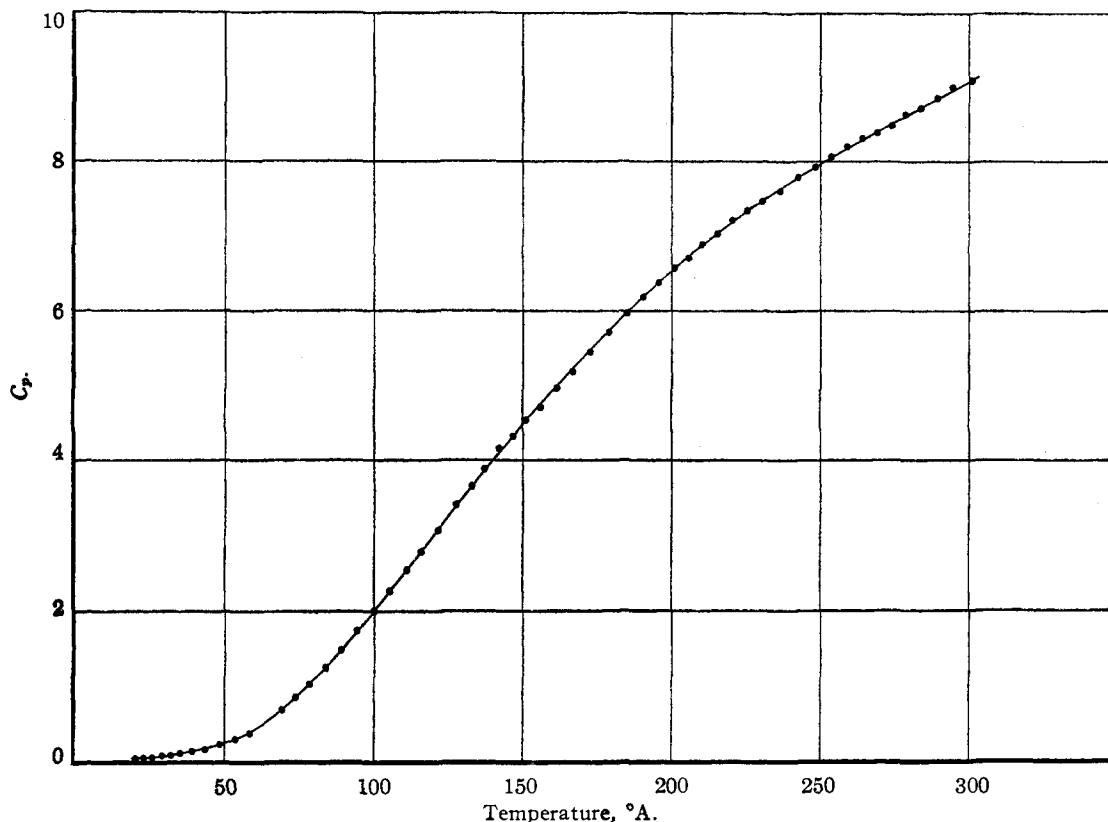


Fig. 2.—Molal heat capacity of magnesium oxide in calories per degree.

The measurements of Parks and Kelley over the range 90–290°K. fall on a smooth curve which lies about 1% below the present observations at ordinary temperatures with the difference increasing by systematically greater amounts at lower temperatures. At 90°K. the deviation has increased to –6%.

We do not question the accuracy of the measurements of Parks and Kelley, since some of their other measurements with the same calorimeter have been substantiated by the work of other observers. Thus the probable cause of the deviation deserves some comment.

The magnesium oxide used by Parks and Kelley had been crystallized from the fused oxide by the Norton Company. It was shown to be pure by analysis. We have learned in a personal communication from Dr. Kelley that cleavage planes of the crystal indicated it to be cubic and rather perfect in character. Also an x-ray investigation on some of the same material had shown typical Laue spot patterns.

As has been mentioned above, the magnesium oxide used in the present investigation was pre-

pared by decomposing the hydroxide in a vacuum at 300–350°. This was considered desirable in order that we might have material in the same state as that in which it was present during the decomposition equilibrium. The material obtained in this manner was of course a powder and it appears that the difference in the results obtained by Parks and Kelley and in this research is due to the difference in the physical state of the material. The low temperature heat capacity results on the very poorly conducting finely divided magnesium oxide are not as accurate as those on the crystalline magnesium hydroxide but it seems probable that the present results on the oxide are too low rather than too high. The fact that the measurements are 6% higher than those of Parks and Kelley on large crystals of magnesium oxide at 90°K. is not so surprising when one considers that the actual difference is a little less than a tenth of a calorie per mole and that some of the molecular restraints must have been weakened on and near the very large amount of surface formed when the magnesium hydroxide was dehydrated.

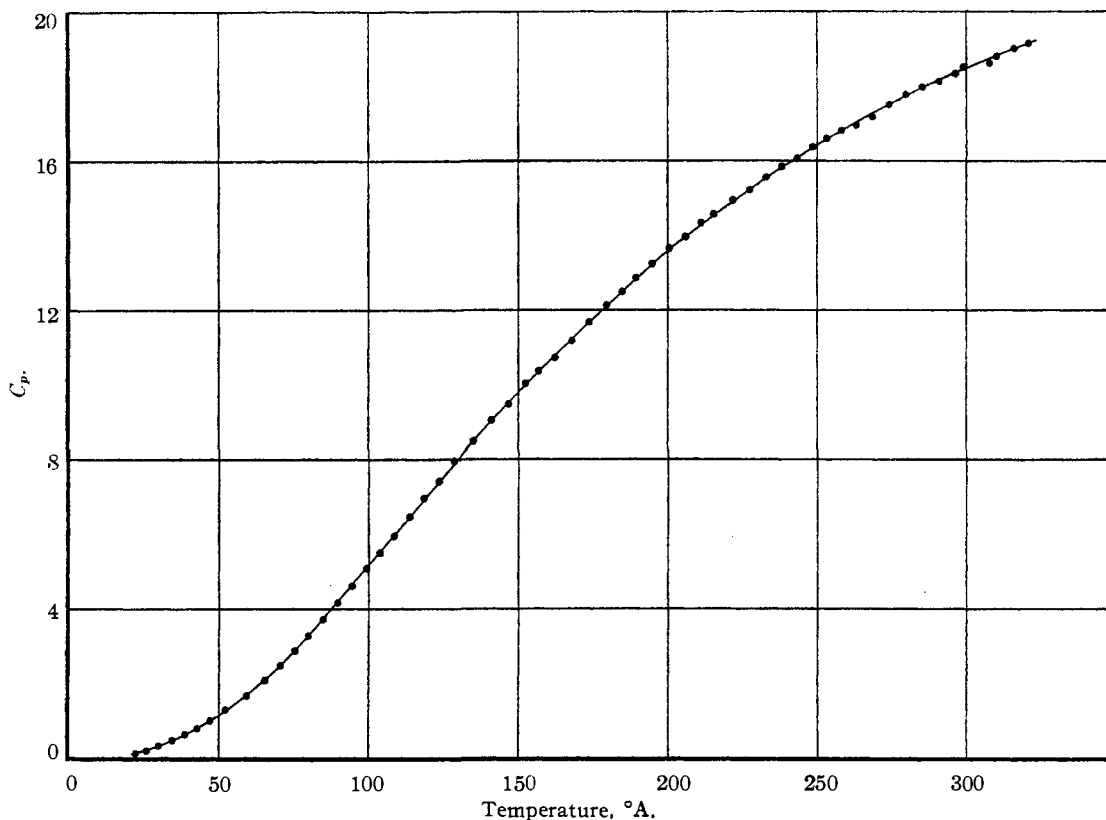


Fig. 3.—Molal heat capacity of magnesium hydroxide in calories per degree.

#### The Heat of Decomposition of Magnesium Hydroxide.—

The heat of the reaction  $\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}(\text{l})$  was determined by measuring the heats of solution of magnesium hydroxide and magnesium oxide in dilute hydrochloric acid.

Figure 4 shows a cross-sectional diagram of the calorimeter used for the measurements of the heats of solution of magnesium oxide and magnesium hydroxide in hydrochloric acid. The apparatus consisted essentially of a dewar vessel equipped with a stirrer, a resistance thermometer and heater combined, and a means of admitting the sample. The one-liter silvered dewar vessel was specially made, without spacing plugs, to minimize heat leak. The resistance thermometer-heater, A, was wound on a platinum tube 2 cm. in diameter and 7 cm. long. It consisted of about 45 ohms of number 40 B. and S. gage double silk-covered copper wire insulated and kept in good thermal contact with the tube by Bakelite lacquer. A thin platinum sheath was put over this and welded around the ends. The leads of number 24 copper wire came through a small platinum tube welded to the inside tube of the thermometer-heater. Potential leads were attached at a point somewhat above the surface of the liquid in the dewar vessel, thus minimizing the effect of the heat generated in the leads. The thermometer-heater was supported by the small platinum tube.

Two different stirrers, B, were used at different times during the work. One was a 10-blade platinum stirrer, the other a 3-blade glass stirrer. These were fastened with

deKhotinsky cement into the stirrer shaft well above the liquid level in the dewar vessel. The stirrer shaft was made from thin German silver tubing to minimize heat conduction. Bearing surfaces were provided only near the ends.

The upper framework of this calorimeter was a heavy support with a series of tubes leading down to the mouth of the dewar vessel. The joint between the support and the dewar was made water tight with adhesive tape and paraffin while the dewar flask was held snugly in place by a metal ring underneath attached to the upper metal part by three cords and a spring. The tubes were used as follows: one for the stirrer shaft; one for the thermometer-heater, E (this tube was filled with paraffin to keep the wires in thermal contact with the tube), and two for the sample tube. These tubes were made long to make sure that all heat leaking into the calorimeter through the various shafts and wires would be from the temperature of the outside bath.

The device for admitting the sample was constructed as follows: A glass tube, C, 5 cm. long and 1.5 cm. outside diameter was ground flat on both ends. A piece of thin gold foil was fastened over one end with paraffin. The sample was then weighed into the tube, after which the other end was sealed with gold foil. This tube was then fastened with adhesive tape and paraffin to one end of a glass rod which passes through one of the tubes in the upper framework of the calorimeter. In placing the dewar flask on the apparatus, the sample tube could be turned under



the stirrer to pass the neck of the flask, then turned out and drawn up to its place beside the resistance thermometer. A pointed glass rod, D, passed through the other tube in the upper part of the apparatus and was held so that its point was about a millimeter directly above the sample tube. When it was desired to dissolve the sample, this glass rod was pushed through both pieces of gold foil, then pulled back to its original position.

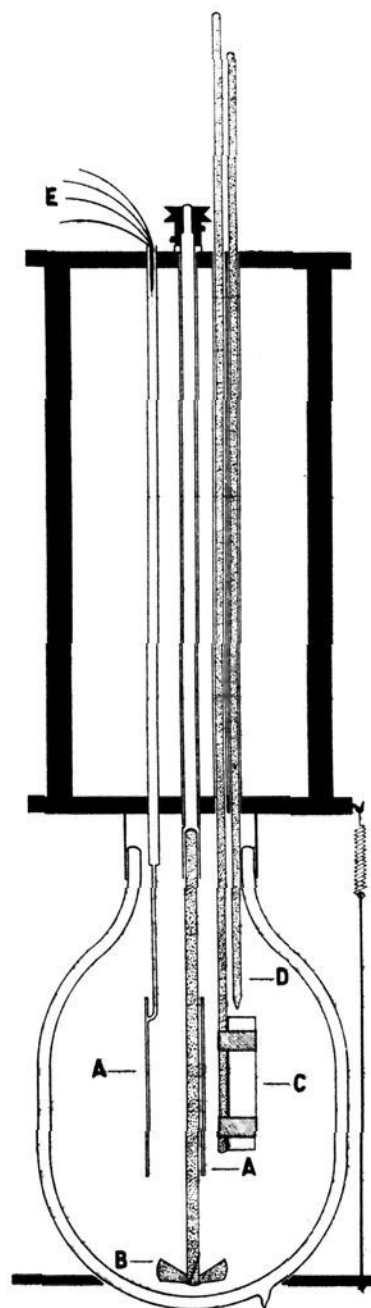


Fig. 4.—Calorimeter used for heat of solution measurements.

The experiments were arranged so that the bath temperature was midway between the initial and final calorimeter temperatures. Perhaps it would have been preferable to keep the calorimeter temperature always below that of the thermostat to eliminate any possibility of distillation heat effects. However, it may be shown that there was practically no tendency for distillation to occur in the present case. The affinity of water for hydrogen chloride is so great that it approximates the properties of a non-volatile solute in dilute solution. The vapor pressure of water over 1 *M* hydrochloric acid is sufficiently below that of pure water so that the solution must be about 0.7° above the

Resistance thermometer measurements were made with a Müller type Wheatstone bridge with a galvanometer of high sensitivity. When the bridge was in balance the current through the resistance thermometer was about 3 m. a. The small amount of heat resulting from the thermometer current was included in the "heat of stirring" correction. The stirrer was driven at constant speed to ensure constancy of this correction factor. The energy used for determining the heat capacity of the calorimeter was supplied by storage cells. The energy measurements were made with a Leeds and Northrup type K potentiometer.

The heat of solution measurements were arranged so that the various concentrations and amounts were the same in the final solution of every experiment. This solution was obtained by adding 5.0000 g. of magnesium hydroxide to 900 cc. of 1.0000 *N* hydrochloric acid. 1.461 g. of water was added to the acid solution before the magnesium oxide measurements.

The thermostat surrounding the calorimeter was kept at about 25°C. and the temperature was recorded to

thermostat temperature before a practicable mechanism for distillation becomes possible.

The correction for heat interchange with the surroundings was made graphically and it was assumed that the thermal leakage was at every instant proportional to the temperature difference between the bath and the calorimeter. The validity of this assumption for the present apparatus and conditions was carefully checked experimentally. Temperature readings were taken at minute intervals during the reaction period and the reaction was considered complete only when the observed rate of temperature change agreed with the value calculated from the known thermal head and the "heat of stirring." The oxide dissolved much more readily than the hydroxide and consequently the runs were shorter. The magnitude of the total heat corrections was about 1% of the heat of solution.

Several heat capacity determinations were made after each heat of solution experiment. These measurements were made with approximately the same temperature increase as that during solution and were made both at lower and higher temperatures so a good interpolated value could be obtained.

The 0.15% (0.22 mole %) potassium impurity is sufficient to require some consideration concerning its possible effect on the results. It may safely be assumed that it was present as potassium hydroxide and it would remain as potassium hydroxide when magnesium oxide was formed from the hydroxide. By coincidence, not only are the molecular weights of potassium and magnesium hydroxides nearly the same but their molal heats of solution are the same within a fraction of a per cent. Thus no appreciable error would have been introduced by ignoring the presence of the potassium hydroxide in the pure magnesium hydroxide, or by counting it as magnesium hydroxide in the magnesium oxide. The heat of solution of magnesium hydroxide to be given later was obtained by making the above assumption. However, in determining the heat of dehydration of magnesium hydroxide we made the better assumption that the heat of solution of the potassium hydroxide would cancel in obtaining the difference of the two experimental values. The experimental values are given in Table IV.

TABLE IV  
HEATS OF SOLUTION OF "Mg(OH)<sub>2</sub>" AND "MgO" IN *M* HCl AT 25°C.

5.0000 g. "Mg(OH)<sub>2</sub>" = 0.085526 mole Mg(OH)<sub>2</sub> + 0.000192 mole KOH. 3.5386 g. "MgO" = 0.081119 mole MgO + 0.004407 mole Mg(OH)<sub>2</sub> + 0.000192 mole KOH. Molecular weights: Mg(OH)<sub>2</sub> = 58.336, MgO = 40.32.

Experiment	"Mg(OH) <sub>2</sub> "	"MgO"
1	2294.2	3084.1
2	2293.5	3082.4
3	2294.7	3085.5
Mean	2294.1	3083.8

From Table IV it is found that the dehydration of 0.081119 mole of magnesium hydroxide requires 3083.8 - 2294.1 = 789.7 cal. The corresponding value is 9735 cal./mole of magnesium hydroxide. From the data of Rossini<sup>16</sup> we estimate that the

(16) Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

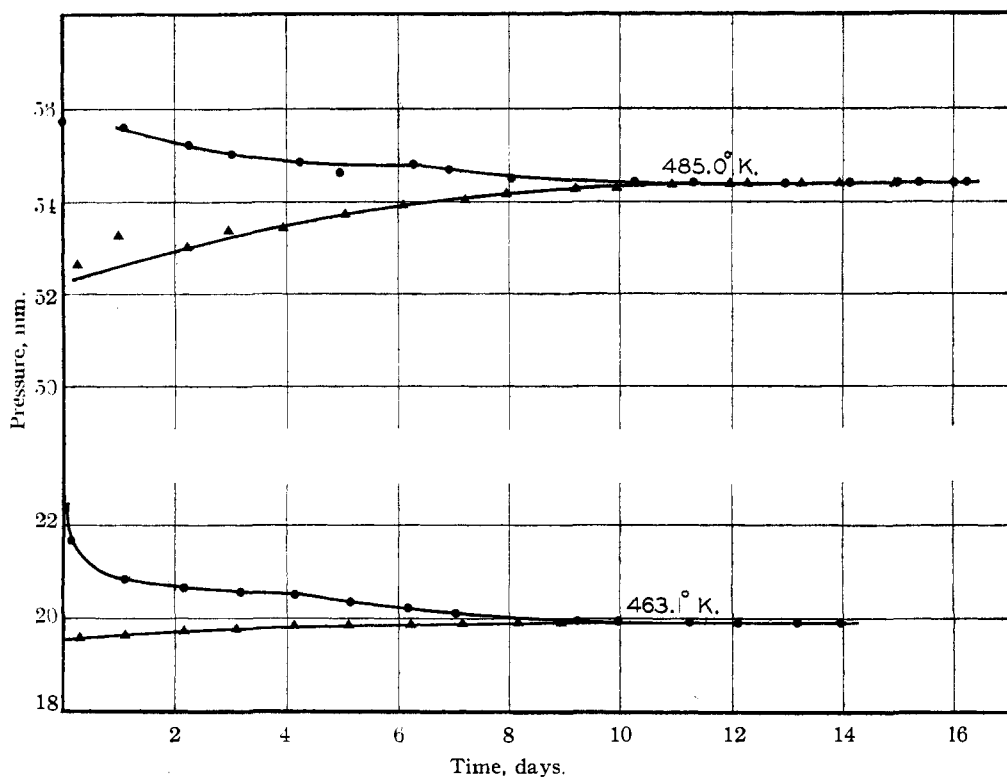
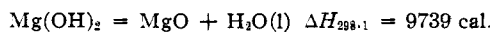
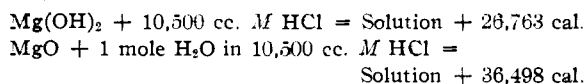


Fig. 5.—The dissociation pressure, showing the approach to equilibrium.

partial molal heat content of water in the final calorimetric solution is  $\frac{1}{2}$  cal. less than that of pure water. Applying this correction



Also



#### The Dissociation Pressure of Magnesium Hydroxide.—

The apparatus used to measure the dissociation pressure of magnesium hydroxide was a manometer, of 1.5-cm. inside diameter glass tubing, with a bulb on one side containing a mixture of magnesium hydroxide and magnesium oxide. The other side of the manometer was connected through a mercury U-trap to a high vacuum system. The manometer, sample bulb and U-trap were kept in a stirred air thermostat which could be kept constant to  $0.1^\circ$  at any temperature up to  $220^\circ\text{C}$ .

Both sides of the manometer and the sample were pumped, by means of a mercury diffusion pump with a liquid air trap in the line. The sample and line were at a temperature of about  $200^\circ\text{C}$ . during the evacuation. The sample bulb side was then sealed off. The mercury could be run up in the U-trap thus allowing the vapor pressure of mercury on the vacuum side of the manometer to balance that on the bulb side. The U-trap also served to prevent distillation of the mercury from the manometer to the vacuum line outside the thermostat. This is an important consideration in cases such as the present one where

the rate of change of pressure due to volume change on the bulb side, because of loss of mercury, would have been of the same order as the rate of change during approach to equilibrium. The difference in height of the mercury menisci was read through a plate glass window by means of a cathetometer accurate to a few hundredths of a mm.

Equilibrium pressures were obtained at  $463.1$  and  $485.0^\circ\text{K}$ . In each case the equilibrium was approached from both higher and lower temperatures. Table V gives the pressures measured during the approach to equilibrium. Each observation given is an average of several measurements. The individual readings did not vary more than  $0.1$  mm. from the average. The pressures are given in international cm. of mercury. In correcting the observations the density of mercury was taken from the "I. C. T."<sup>17</sup> The standard acceleration of gravity was taken as  $980.665$  cm./sec.<sup>2</sup>. The gravitational acceleration at this location has been determined by Sternwarte<sup>18</sup> as  $979.973$  cm./sec.<sup>2</sup>. The data are represented graphically in Fig. 5.

The first flat portion in the curves approaching equilibrium from high pressures is attributable to adsorption. That this might easily have been mistaken for true equilibrium is shown by the following experiment. During some preliminary measurements the apparatus was cooled while the approach to equilibrium was in the adsorption stage. On return to the original temperature there was a return to the false equilibrium value and later a decrease to

(17) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926.

(18) Sternwarte, Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Verlag Julius Springer, Berlin, 1928.

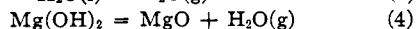
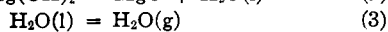
the true equilibrium pressure. It is quite evident that approach to the same pressure from each side of an equilibrium is not a sufficient criterion of true equilibrium. The effect is so insidious that we have little doubt that many such errors have occurred in the study of equilibria. A case in point are the previous data<sup>19</sup> on the dissociation pressure of magnesium hydroxide. These measurements are so badly in error that we were led to believe that the dissociation pressure could be measured conveniently at temperatures obtainable with a water thermostat and we set up such an apparatus. It soon became clear that the dissociation pressure measurements of Johnston over the system magnesium hydroxide and magnesium oxide were in reality adsorption pressures and calculation of the heat of reaction from the data showed a value of the same order as the heat of vaporization of water.

TABLE V

DISSOCIATION PRESSURES OF Mg(OH) <sub>2</sub>							
Approaching equilibrium from low pressures				Approaching equilibrium from high pressures			
463.1°K.		485.0°K.		463.1°K.		485.0°K.	
Time, days	P inter. cm.	Time, days	P inter. cm.	Time, days	P inter. cm.	Time, days	P inter. cm.
0.29	1.954	0.25	5.263	0.13	2.164	0	5.570
1.08	1.964	.96	5.326	1.08	2.082	1.08	5.558
2.13	1.971	2.21	5.301	2.15	2.064	2.25	5.522
3.08	1.976	2.96	5.336	3.17	2.055	3.00	5.503
4.13	1.983	3.94	5.341	4.17	2.049	4.25	5.485
5.08	1.985	5.04	5.371	5.15	2.033	4.96	5.462
6.21	1.987	6.08	5.391	6.17	2.022	6.29	5.481
7.13	1.989	7.19	5.401	7.04	2.009	6.92	5.472
8.13	1.991	7.96	5.416	9.21	1.994	8.04	5.448
8.96	1.991	9.21	5.426	9.96	1.994	10.25	5.441
		9.94	5.426	11.21	1.991	11.29	5.437
		10.94	5.436	12.08	1.991	12.96	5.439
		11.96	5.439	13.13	1.991	14.13	5.439
		12.27	5.438	13.96	1.991	15.00	5.439
		13.25	5.440			15.37	5.438
		13.92	5.437			16.00	5.439
		14.87	5.439			16.25	5.439
Equil. values	1.991		5.439		1.991		5.439

### Thermodynamic Treatment of the Data.—

Various thermodynamics quantities of interest to the experiment are tabulated in Table VI. They were obtained from data relating to the reactions



$\Delta F^\circ = -RT \ln K$  where  $K$  is the vapor pressure (in atm.) of water in equation 3 and the dissociation pressure (in atm.) in equation 4.

$$\Delta H_T = \Delta H_{298.1} + \int_{298.1}^T \Delta C_p \, dT$$

$$\Delta S_T = (\Delta H - \Delta F)/T$$

$$\Delta S_{298.1} = \Delta S_T - \int_{298.1}^T \Delta C_p \, d \ln T$$

(19) Johnston, *Z. physik. Chem.*, **62**, 330 (1908).

The heat of vaporization of water at 298.1°K.,  $\Delta H$  of equation 3, has been estimated as 10,499  $\pm$  3 cal. per mole by Giauque and Stout<sup>2</sup> after a consideration of the very accurate available data which have been reviewed by Flock.<sup>20</sup>

Thermodynamic quantities including the heat content and entropy of gaseous water have been calculated from spectroscopic data by Gordon<sup>21</sup> and these values were used where necessary. However, corrections for the rotational deformation of the water molecule were applied to Gordon's values in accordance with the calculations of Wilson.<sup>22</sup>

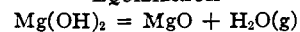
The entropies of magnesium hydroxide and oxide were obtained from the third law of thermodynamics by graphical integration of the heat capacity data

$$S = \int_0^T C_p \, d \ln T$$

Since the heat capacity of magnesium hydroxide was extrapolated for about 150° above the last measurement, at 320°K., the probable error due to this assumption requires comment. While we believe the extrapolation is reliable, we wish to point out that considerable error in the assumed values would produce little effect in the final result. For example let us consider the effect of an error of one calorie per degree in the assumed heat capacity at 475°K. The curve at 320°K. gives direction as well as value to the curve above that temperature, thus a reasonable type of deviation would be given by a proportionality to the square of the temperature difference above 320°K. Since the same heat capacity values are used for calculating differences in heat content and in entropy the effect of an error in the assumed heat capacity values largely cancels. It may be shown that a deviation of the above type will increase the derived entropy of water by approximately 0.01 cal./deg. per mole for each increase of one calorie per degree in the

TABLE VI

SOME THERMODYNAMIC QUANTITIES RELATED TO THE EQUILIBRIUM



T, °K.	$\Delta F$	$\Delta H$	$\Delta S$	MgO, $S_T$	Mg(OH) <sub>2</sub> , $S_T$	H <sub>2</sub> O, $S_T$ Exptl.	H <sub>2</sub> O, $S_T$ Spect.
485.0	2541	19,689	35.36	11.47	25.22	49.11	49.10
463.1	3351	19,783	35.48	10.98	24.15	48.65	48.72
298.1	9297	20,238	36.67	6.66	15.09	45.10	45.13

(20) Flock, *Bur. Standards J. Research*, **5**, 481 (1930).

(21) Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

(22) Wilson, *ibid.*, **4**, 526 (1936).



heat capacity of magnesium hydroxide at 475°K. Thus error introduced by the extrapolation can be estimated at not more than a few hundredths of an entropy unit.

The experimental entropy value given for 298.1°K. was calculated from an average of the measurements at 463.1 and 485.0°K.

As may be seen from the comparisons in the last two columns of Table VI the third law values of the entropy of water are in excellent agreement with those calculated from the band spectrum data.

We thank Dr. Roy Overstreet for analyzing the magnesium hydroxide used in the above experiments.

### Summary

The heat capacities of magnesium oxide and magnesium hydroxide have been measured from 20 to 300°K. and 20 to 320°K., respectively.

Evidence has been presented to show that the low temperature heat capacity of magnesium oxide prepared by the decomposition of magnesium hydroxide at 300–350°C. is definitely greater than the heat capacity of crystalline material prepared from the fused oxide.

The dissociation pressure of the system Mg(OH)<sub>2</sub>, MgO has been measured accurately at 463.1 and 485.0°K. The pressures found were 1.991 and 5.439 international cm., respectively.

During the dissociation measurements it was found that an approach to the equilibrium from the high temperature side was at first accompanied by a slowly obtained false equilibrium pressure due to surface adsorption of the water. If the substance was cooled at this stage it was possible to approach the same false equilibrium from the low temperature side. It is evident that this usual experimental criterion for true

equilibrium in such cases is by no means a safe one.

It is suggested that dissociation equilibria should be first approached from the low temperature side. Subsequent attainment of the same value from the high temperature direction may be taken as substantial evidence of true equilibrium.

The heat of solution of one mole of magnesium hydroxide in 10,500 cc. of molal hydrochloric acid was found to be 26,763 calories at 25°C.

The heat of solution of one mole of magnesium oxide in 10,500 cc. of molal hydrochloric acid +1 mole of water was found to be 36,498 calories at 25°C.

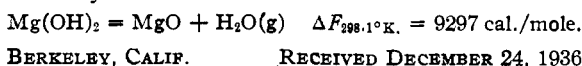
These measurements when corrected for the partial molal heat content of water in the solution lead to a value of  $\Delta H_{298.1^\circ\text{K.}} = 9738$  cal. for the dissociation of one mole of magnesium hydroxide to give magnesium oxide and pure liquid water.

The above data have been used with the third law of thermodynamics to calculate the molal entropy of gaseous water at 485.0, 463.1 and 298.1°K. The values obtained are 49.11, 48.65 and 45.10 cal./deg., respectively.

These may be compared with values obtained with the assistance of the band spectrum data for water. The values for corresponding temperatures are 49.10, 48.72 and 45.13 cal./deg., respectively.

The excellent agreement constitutes one of the best pieces of evidence in support of the third law of thermodynamics and of the results of quantum statistics.

The free energy for the dissociation of magnesium hydroxide is



BERKELEY, CALIF.

RECEIVED DECEMBER 24, 1936