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STUDIES OF HEAT OF SOLUTION OF CALCIUM AND MAGNESIUM OXIDES AND HYDROXIDES

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ABSTRACT

The heat evolved in the solution of MgO in hydrochloric acid was found to decrease as the temperature at which the MgO was prepared was increased. This is shown in the following equations, where the values given are those of ΔH , the increment in the heat content. The negative sign, therefore, indicates the evolution of heat.

MgO(c) [prepared by dehydrating Mg(OH)₂ for 2.5 hours at 450° C] + 17,630 g of 2.085 M HCl = solution; $\Delta H_{298.1^\circ K} = -36.67 \pm 0.07$ kcal, and

MgO(c) [prepared by dehydrating Mg(OH)₂ for 2.5 hours at 1,425° C] + 17,630 g of 2.085 M HCl = solution; $\Delta H_{298.1^\circ K} = -35.72 \pm 0.03$ kcal.

The decrease in the heat evolved is ascribed mainly to an increase in the particle size of the MgO as the temperature of ignition was increased. Since X-ray diffraction patterns were similar there appeared to be no change in crystalline form. The increase in particle size was indicated by a decrease in the rate of solution in the calorimeter and was verified by sedimentation experiments. Heat values have also been obtained for the solution of Mg(OH)₂, CaO, and Ca(OH)₂ in hydrochloric acid. Heat of hydration of MgO and CaO was calculated from heat-of-solution data. The heat of hydration of MgO to Mg(OH)₂ depends on the characteristic properties of both the MgO and Mg(OH)₂. Heat of hydration of CaO to Ca(OH)₂ was also determined by direct hydration of CaO in a solution saturated with respect to Ca(OH)₂.

CONTENTS

	Page
I. Introduction.....	133
II. General procedure.....	134
III. Apparatus and materials.....	135
IV. Effect of the temperature of ignition on the heat of solution of MgO in hydrochloric acid.....	135
1. Experimental.....	135
2. Corrections.....	138
(a) Corrections to common concentrations.....	138
(b) Correction to a temperature of 25° C.....	142
V. Heat of solution of Mg(OH) ₂ in hydrochloric acid.....	143
VI. Heats of solution of CaO and Ca(OH) ₂ in hydrochloric acid.....	144
VII. Heats of hydration of MgO and CaO.....	145
VIII. Summary.....	147
IX. References.....	148

I. INTRODUCTION

In a recent investigation at the National Bureau of Standards of the hydration of magnesia in dolomitic limes and putties [1]¹ it was

¹ Figures in brackets here and elsewhere throughout the text indicate the literature references at the end of this paper.

necessary to determine the heats of solution of MgO , $\text{Mg}(\text{OH})_2$, CaO , and $\text{Ca}(\text{OH})_2$ in hydrochloric acid. Since the values were to be used only for the purpose of ascertaining the percentage of MgO in dolomitic hydrated limes and putties, several minor corrections which were not significant in that determination were omitted. Furthermore, the data in that paper pertain only to calcium oxide and magnesium oxide ignited at temperatures roughly approximating those at which dolomitic limes are burned in practice. It has been found in this laboratory that the heat of solution of magnesium oxide depends appreciably on the temperature of ignition prior to its solution. This paper describes the variation in the heat of solution of MgO and includes data on the heats of solution of $\text{Mg}(\text{OH})_2$, CaO , and $\text{Ca}(\text{OH})_2$ in addition to those given previously [1].

II. GENERAL PROCEDURE

In the preparation of MgO and CaO for the determination of heats of solution, samples of $\text{Mg}(\text{OH})_2$ and CaCO_3 were ignited, cooled to room temperature in a desiccator, and immediately weighed and sealed in the sample container of the calorimeter. The MgO , when not sealed, was found to take up moisture rapidly for 10 or 15 minutes after its removal from the desiccator. Since CaO also increases in weight upon exposure to air under ordinary conditions, it was desirable to make weighings of these materials as rapidly as possible. For this reason no attempt was made to take samples of exactly the same weight although equal weights of acid solution were used in the different experiments. Such a procedure produces differences in the concentrations of the constituents of the final calorimetric solutions. Corrections have been made for these variations, although they are relatively small in the experiments described in this paper.

Heat-capacity measurements were made by adding definite amounts of electrical energy to the calorimeter plus the initial hydrochloric acid solution rather than to the calorimeter plus the final more complex solutions. The heat capacities of the samples [4, 5] were therefore added to that of the calorimeter containing the initial acid solution, and the heat-of-solution values corrected to a final temperature of 25°C . This procedure gives the heat of the isothermal reaction at 25°C .

The "energy equivalent error" [18], a , (three times the "probable error") of the heat-capacity measurements of the calorimeter was calculated by the formula

$$a = \pm (100) \frac{2\sqrt{\Sigma\Delta^2/m(m-1)}}{(\text{value of energy equivalent})} \text{percent,}$$

where $\Sigma\Delta^2$ is the sum of the squares of the m deviations from the arithmetical average of the experimental values.

Likewise, the "reaction error", b , was calculated by the formula

$$b = \pm (100) \frac{2\sqrt{\Sigma\Delta^2/n(n-1)}}{(\text{value of reaction energy})} \text{percent,}$$

where n is the number of determinations of the heat of solution.

The final assigned "precision error" of the average value for the heat of solution is

$$\text{"precision error"} = \pm \sqrt{a^2 + b^2} \text{ percent.}$$

The last equation was also used to calculate the error of the sum or difference of two heats of solution *A* and *B* affected with errors *a* and *b*, but the errors in this case must be expressed in calories and not in percent. The final change back to percent was made after the addition or subtraction was completed and the magnitudes of both the error and desired quantity were known.

The unit of energy employed in this work is the National Bureau of Standards International Joule, and conversion to a defined or conventional calorie is made by using the factor 1/4.1833. See reference [18] for further information on this point.

III. APPARATUS AND MATERIALS

The calorimeter used in this work has been adequately described in previous publications [2]. The temperature of the water surrounding the outside jacket of the calorimeter was maintained at $25 \pm 0.005^\circ \text{C}$.

The hydrochloric acid solutions were prepared from concentrated acid of analytical reagent quality and distilled water.

Two samples of magnesium hydroxide were used. The first was naturally occurring brucite which was completely soluble in hydrochloric acid, free of silica, and contained only traces of calcium, iron, and aluminum oxides. The second sample was prepared from magnesium oxide of analytical reagent quality. Before being used, the oxide was extracted with water to remove any water-soluble substance with which it might be contaminated. An analysis then showed that it was completely soluble in hydrochloric acid, free of chlorides and sulfates, and contained only traces of iron and aluminum oxides. In the preparation of magnesium hydroxide, this oxide was ignited in a muffle furnace for several hours at 850°C , hydrated with steam in an autoclave for 2 hours at a pressure of 120 lb/in.², and then oven-dried for 1 hour at 105°C .

The magnesium oxide used in all determinations of heat of solution was obtained by dehydrating the above prepared magnesium hydroxide at the desired temperature.

Calcium carbonate of analytical reagent quality was used in the preparation of calcium oxide and calcium hydroxide. The carbonate was completely soluble in hydrochloric acid, free of chlorides, sulfates, and silicates, and contained only traces of iron and aluminum oxides. Calcium oxide was obtained by igniting the carbonate for about 4 hours over a Meeker burner just prior to each determination of heat of solution. The ignition temperature was $1,050^\circ$ to $1,100^\circ \text{C}$. In the preparation of calcium hydroxide, the carbonate was ignited in a muffle furnace for several hours at 950°C and then hydrated and dried as in the preparation of magnesium hydroxide.

IV. EFFECT OF THE TEMPERATURE OF IGNITION ON THE HEAT OF SOLUTION OF MgO IN HYDROCHLORIC ACID

1. EXPERIMENTAL

Experimental evidence indicates that in some instances the heat of solution of a material is markedly affected by the manner in which it is prepared. Thus, Fricke, Schnobel, and Beck [3], by varying the method of preparation of $\text{Mg}(\text{OH})_2$, obtained differences in its heat

of solution in 3.75 *N* HCl of as much as 850 cal per mole. Newman and Wells [2] have reported differences in the heat of solution (in 2.09 *M* HCl) of the stable form of CaSO_4 prepared by dehydrating $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at various temperatures, and for various periods of time at the same temperature. These differences have been attributed to differences in surface rather than to any fundamental change in the internal structure of the crystals.

It is well known that the apparent density of MgO increases appreciably upon ignition at increasingly higher temperatures. Therefore, it seemed reasonable that its heat of solution might be affected by the temperature at which it had been ignited previous to a determination. This was further suggested by the discrepancy in the heat of hydration of MgO prepared by dehydrating $\text{Mg}(\text{OH})_2$ at 1,050° to 1,100° C, as determined in this laboratory [1], and that of MgO prepared

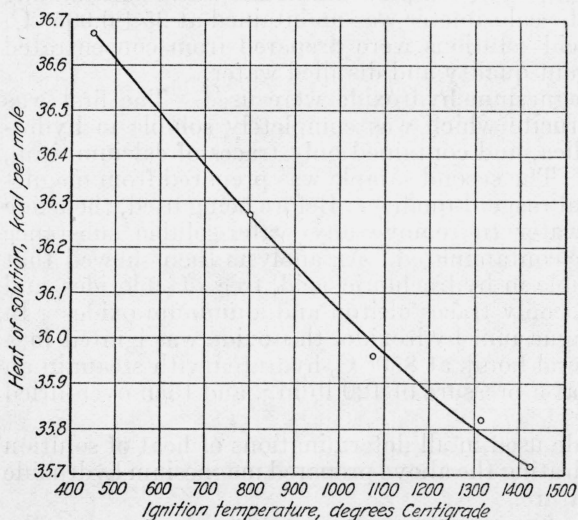


FIGURE 1.—Curve showing the decrease in heat of solution of MgO prepared by heating $\text{Mg}(\text{OH})_2$ for 2.5 hours at increasing temperatures.

Five heat-capacity measurements made by adding definite amounts of electrical energy to the calorimeter plus 640 g of 2.085 molal² HCl solution gave the values 648.1, 648.4, 648.4, 648.0, and 648.6 cal, respectively, or an average of 648.3 cal with the "energy equivalent error" = ± 0.2 cal.

Table 1 shows that $\text{Mg}(\text{OH})_2$ was not completely dehydrated in 2.5 hours at 450° C or 800° C. From the known heat of solution of $\text{Mg}(\text{OH})_2$, the heat of solution of MgO in these samples was corrected for the amount of hydroxide present. Samples used in experiments 1 and 2, determination A, represent separate ignitions of $\text{Mg}(\text{OH})_2$. In the same way, the sample used in experiment 1, determination B, differs from that used in experiments 2 and 3 of this determination.

From figure 1 it appears probable that at temperatures higher than 1,425° C the effect of the temperature of ignition on the heat of

by igniting $\text{Mg}(\text{OH})_2$ at 300° C, as determined by Giauque and Archibald [4].

In order to study the effect of ignition temperature on the heat of solution of MgO, determinations of heat of solution were made on samples of MgO prepared by heating $\text{Mg}(\text{OH})_2$ for 2.5 hours at temperatures ranging from 450° to 1,425° C. Data relative to these experiments are given in table 1. The variation of heat of solution with ignition temperatures may also be seen in figure 1.

² The term "molal" (abbreviated *M*) in this paper refers to 1 gram-formula weight in 1,000 g of water

solution of MgO would be less than at lower temperatures. In this connection, the heat of solution of periclase (fused MgO) would be of interest. However, it has been found that as MgO is ignited at higher temperatures, it becomes increasingly difficult to dissolve in hydrochloric acid. Samples of periclase, even when ground to pass a standard No. 325 sieve, did not completely dissolve when stirred in the calorimeter for 3 hours (at 25° C) in 4.355 M hydrochloric acid.

TABLE 1.—Heat of solution of samples of MgO prepared from Mg(OH)₂ by ignition for 2.5 hours at various temperatures, using 640 g of 2.085 M HCl in each experiment

[Heat capacity of calorimeter containing the initial acid solution equals 648.3±0.2 cal.]

Determination	Temperature at which MgO was prepared	Experiment	Weight of sample as MgO	Corrected temperature rise	Final temperature to nearest 0.01°	Ignition loss of sample	Uncorrected heat of solution		Corrected heat of solution of MgO(c)+17.630 g of 2.085 M HCl=solution; $\Delta H_{298.1^\circ K}$	
							ΔH	ΔH		
	°C		g	°C	°C	%	cal/g	cal/mole	kcal	
A	450	{	1	1.3144	1.8107	25.85	2.80	-909.0	-----	-----
			2	1.2547	1.7282	25.90	3.12	-910.6	-----	-----
		Average	-----	1.2845	1.7694	25.88	2.96	-909.8	-36,683	-36.67±0.07
B	800	{	1	1.4986	2.0679	26.01	0.89	-899.7	-----	-----
			2	1.2366	1.7045	25.93	1.00	-899.2	-----	-----
		3	1.6554	2.2822	26.13	1.00	-899.6	-----	-----	
Average	-----	1.4635	2.0182	26.02	0.96	-899.5	-36,268	-36.27±0.02		
C	1,075	{	1	1.8218	2.4998	26.38	-----	-891.5	-----	-----
			2	1.4365	1.9744	26.02	-----	-891.5	-----	-----
		3	1.5968	2.1930	26.10	-----	-890.8	-----	-----	
Average	-----	1.6193	2.2224	26.17	-----	-891.3	-35,937	-35.96±0.02		
D	1,315	{	1	1.7325	2.3714	26.20	-----	-888.0	-----	-----
			2	1.8511	2.5318	26.39	-----	-887.3	-----	-----
		Average	-----	1.7918	2.4516	26.30	-----	-887.7	-35,792	-35.82±0.03
E	1,425	{	1	1.6351	2.2314	26.11	-----	-885.2	-----	-----
			2	1.4755	2.0148	26.19	-----	-885.7	-----	-----
		Average	-----	1.5553	2.1231	26.15	-----	-885.5	-35,703	-35.72±0.03

Although a comprehensive study was not made of this phase of the problem, it appears probable that the time of ignition also affects the heat of solution of MgO. It seems, however, that relatively large differences in time are necessary before this effect becomes significant, as is indicated by the data of table 2. The heat of solution of MgO heated for 18 hours at 800° C (table 2) is an average of two determinations which differed by 1.3 cal/g; that of the MgO heated for 4 hours at 1,075° C is an average of four determinations which differed by a maximum of 1.5 cal/g.

The differences in the heat of solution of MgO, as shown in tables 1 and 2, are ascribed mainly to differences in surface. X-ray diffraction patterns were similar, indicating no change in crystalline form. An increase in temperature of ignition resulted in a decrease in the rate of solution in the calorimeter, and, as is well known, it also is followed by a decrease in the rate of hydration. Both effects can be explained by an increase in particle size. Sedimentation experiments in anhydrous normal butyl alcohol showed that the sample of MgO heated at 800° C contained considerable material less than 1 micron

in diameter, and that much of this in turn was less than 0.5 micron. On the other hand, the MgO heated at 1,315° C had very little material finer than 1 micron.

TABLE 2.—*Effect of time of ignition on the heat of solution of MgO in hydrochloric acid*

Temperature of ignition at which MgO was prepared	Time of ignition	Corrected heat of solution of MgO (c)+17,630 g of 2.085 M HCl=solution; $\Delta H_{298.1^\circ K}$ equals:
	<i>Hours</i>	<i>kcal</i>
800° C.....	{ 2.5	-36.27 ±0.02
	{ 18.0	-35.99 ±0.05
1,075° C.....	{ 2.5	-35.96 ±0.02
	{ 4.0	-35.94 ±0.06

2. CORRECTIONS

By means of several minor corrections the various average heats of solution were reduced to a comparable basis and expressed as the heats of a definite chemical reaction in which the only variable was the temperature at which the MgO was ignited. These values are shown in the last column of table 1.

In making corrections, the following factors were considered:

- (1) Variation of the concentration of MgCl₂ in the final solutions;
- (2) variation of the concentration of HCl in the final solutions; and
- (3) variation of the final temperature from 25° C.

(a) CORRECTIONS TO COMMON CONCENTRATIONS

The first two factors are concerned with concentrations in the calorimetric solutions. These concentrations are shown in table 3. Inasmuch as they differed, all determinations were corrected so that they were on a basis equivalent to that of determination B for which the equation in the last column of table 1 was written.

TABLE 3.—*Concentration conditions of the calorimetric solutions before and after samples of MgO have been dissolved*

Determination	Concentration conditions in the original solution		Concentration conditions in the final solution		
	Amount of HCl	Concentration of HCl	Amount of HCl	Concentration of HCl	Concentration of MgCl ₂
	<i>Moles per mole of MgO</i>	<i>Moles per 1,000 g of H₂O</i>	<i>Moles per mole of MgCl₂</i>	<i>Moles per 1,000 g of H₂O</i>	<i>Moles per 1,000 g of H₂O</i>
1.....	38.9314	2.0852	36.9314	1.9761	0.0535
2.....	34.1698	2.0852	32.1698	1.9610	.0610
3.....	30.9013	2.0852	28.9013	1.9479	.0674
4.....	27.9089	2.0852	25.9089	1.9331	.0746
5.....	32.1530	2.0852	30.1530	1.9533	.0648

The last column of table 3 shows the concentration of MgCl₂ in the final solutions. The corrections to be applied for the differences shown in this column are, therefore, the heats of dilution or of concentration of a mole of MgCl₂ from the various concentrations to a

concentration of 0.0610 *M*. Expressed in other words, they are the differences in the apparent molal heat content of MgCl_2 in a 0.0610 *M* solution and in solutions of the other concentrations. However, the effect of concentration on the apparent molal heat content should be determined in approximately 2 *M* HCl rather than in water alone since the former represents the experimental conditions. That the concentration effects differ decidedly under the two conditions may be seen from figure 2, which shows the effect of concentration on the

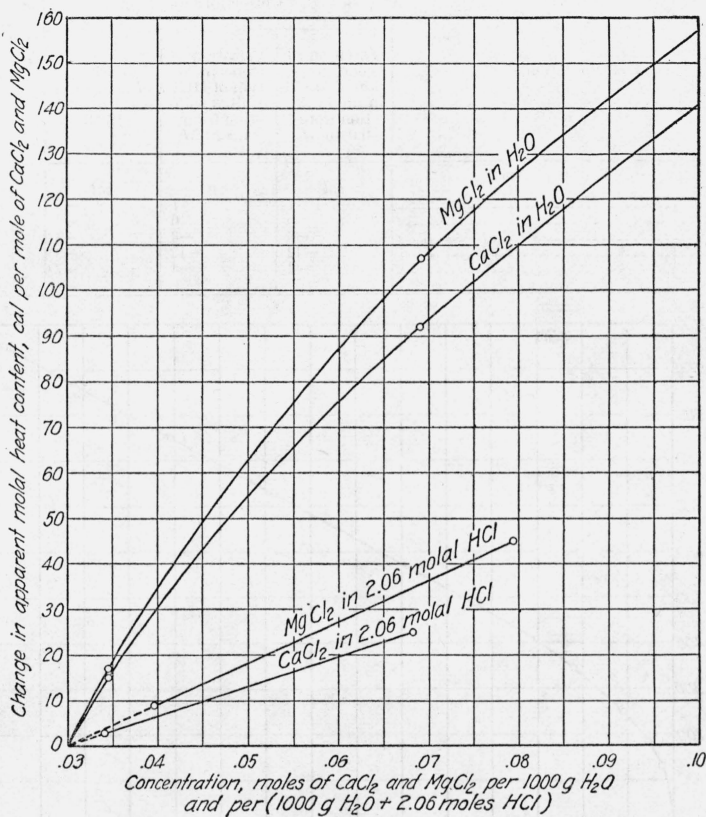


FIGURE 2.—Curves showing the changes in apparent molal heat content of CaCl_2 and MgCl_2 as functions of their concentrations in water and a hydrochloric acid solution.

The curves for MgCl_2 and CaCl_2 in water were drawn from data given by Bichowsky and Rossini, *Thermochemistry of Chemical Substances*, p. 113 and 117, Reinhold Publishing Corporation, New York, N. Y., 1936, and corrected from 18° to 25° C.

change of the apparent molal heat content of MgCl_2 and CaCl_2 in water and in 2.06 *M* HCl at 25° C. The curves for MgCl_2 and CaCl_2 in water were drawn from reliable data found in the literature [5] and corrected from 18° to 25° C. The graphs for MgCl_2 and CaCl_2 in hydrochloric acid represent values obtained in this laboratory. As the two latter graphs each represent only two experimental points, they were drawn as straight lines although it is probable that they deviate from such.

By means of the curve in figure 2 showing the effect of concentration on the apparent molal heat content of MgCl_2 in 2.06 M HCl , the concentrations of MgCl_2 in the final calorimetric solutions were corrected to a molality of 0.0610. These corrections are shown in the second column of table 4.

TABLE 4.—Corrections of ΔH for the solution of 1 mole of MgO in 2.0852 M hydrochloric acid

Determination	Corrections for—			Total correction cal
	Variation of concentration of MgCl_2 in final solution from 0.0610 M	Variation of concentration of HCl in final solution from 1.9610 M	Variation of final temperature from 25°C	
A.....	cal 7	cal 7	cal -5	cal 9
B.....	0	0	-6	-6
C.....	-6	-6	-7	-19
D.....	-12	-12	-8	-32
E.....	-4	-4	-7	-15

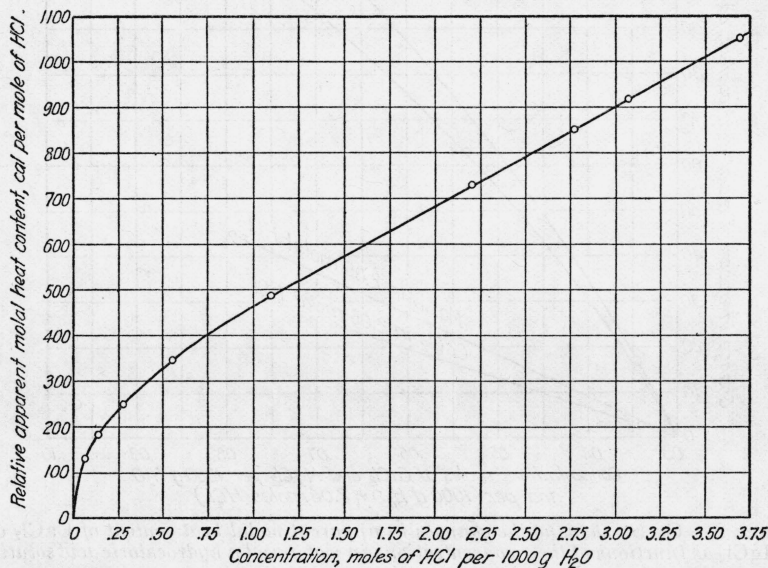


FIGURE 3.—Relation between the relative apparent molal heat content of HCl and concentration.

Drawn from data of Rossini, BS J. Research S 9, 678 (1932) RP499.

When 1 mole of MgO dissolves in a solution of hydrochloric acid, 2 moles of HCl disappear from the solution and 1 mole of H_2O is added. This results in the dilution of the solution which now contains $(n-2)$ moles of HCl , where n is the number of moles of HCl in the original acid solution per mole of MgO added. Since the weight of the samples of MgO differed the number of moles of HCl in the solutions which were diluted in the determinations differed as did also the extent of dilution. From calculations of ΔH for the dilution which took place

in the hydrochloric acid solutions (disregarding for the time being the effect of MgCl_2 in these solutions) the final corrections necessary to make all determinations comparable, so far as concentrations are concerned, can be applied.

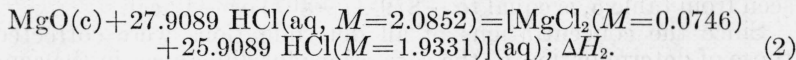
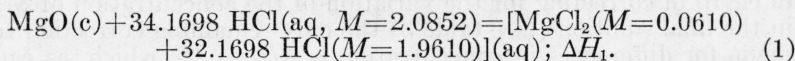
In order to calculate these heats of dilution it is necessary to know: (1) The number of moles of HCl involved in each determination; (2) the extent of dilution; and (3) the variation of the apparent molal heat content of HCl in aqueous solutions with concentration at the temperature and in the concentration range under consideration. The last factor is shown in figure 3, which has been drawn from data of Rossini [6]. From figure 3 it may be seen that at concentrations of about 2 M and at a temperature of 25° C, the apparent molal heat content of HCl changes approximately 220 cal for a change of 1 in molality. Column 4 of table 3 shows the number of moles of HCl diluted in the various determinations. The extent of dilution is obtained by subtracting each of the numbers in column 5 of table 3 from 2.0852, the concentration of HCl in the original acid solution. The product of these three factors is the heat produced by the dilution of the acid solution (neglecting the MgCl_2) when 1 mole of MgO is dissolved. These heats of dilution are shown in table 5.

It should be pointed out that although these solutions contain MgCl_2 in various amounts, corrections have already been made for the differences in the apparent molal heat content of the MgCl_2 (see table 4). The presence of MgCl_2 should, therefore, be disregarded in this method of correcting for differences in the concentration of HCl in the final solutions as will be apparent on consideration of the equations which follow.

TABLE 5.—Heat absorbed by the dilution of the hydrochloric acid solution disregarding the MgCl_2 formed when 1 mole of MgO is dissolved

Determination	Reaction	$\Delta H_{298.1^\circ\text{K}}$
		<i>cal</i>
A	36.9314 HCl(aq, $M=2.0852$) = 36.9314 HCl(aq, $M=1.9761$)	-886
B	32.1698 HCl(aq, $M=2.0852$) = 32.1698 HCl(aq, $M=1.9610$)	-879
C	28.9013 HCl(aq, $M=2.0852$) = 28.9013 HCl(aq, $M=1.9479$)	-873
D	25.9089 HCl(aq, $M=2.0852$) = 25.9089 HCl(aq, $M=1.9331$)	-867
E	30.1530 HCl(aq, $M=2.0852$) = 30.1530 HCl(aq, $M=1.9533$)	-875

Equations 1 and 2 pertain to determinations *B* and *D*, respectively.



It will be assumed for the time being that the samples of MgO have been prepared in the same way and that the environments of the two determinations are comparable in all respects except for concentration. The difference in the heats of the two reactions, $\Delta H_1 - \Delta H_2$, therefore, represents the amount that must be added to ΔH_2 to correct the conditions of determination *D* to those of determination *B*.

Subtracting eq 2 from eq 1 and transposing terms there is obtained

$$\begin{aligned} & 34.1698 \text{ HCl(aq, } M=2.0852) + [\text{MgCl}_2(M=0.0746) \\ & \quad + 25.9089 \text{ HCl}(M=1.9331)](\text{aq}) \\ = & [\text{MgCl}_2(M=0.0610) + 32.1698 \text{ HCl}(M=1.9610)](\text{aq}) \\ & + 27.9089 \text{ HCl(aq, } M=2.0852); \Delta H_3 = \Delta H_1 - \Delta H_2. \end{aligned} \quad (3)$$

From an inspection of figure 2 it may be seen that the apparent molal heat contents of 0.0746 and 0.0610 M MgCl_2 in approximately 2 M HCl differ by about 12 cal (40–28, approximately). Making the appropriate correction in the heat of the reaction as indicated by this approximate value, the two moles of MgCl_2 may be omitted from eq 3 and the reaction written as

$$\begin{aligned} & 34.1698 \text{ HCl(aq, } M=2.0852) + 25.9089 \text{ HCl(aq, } M=1.9331) \\ = & 32.1698 \text{ HCl(aq, } M=1.9610) + 27.9089 \text{ HCl(aq, } M=2.0852); \\ & \Delta H_4 = \Delta H_3 + 12 \text{ cal} = \Delta H_1 - \Delta H_2 + 12 \text{ cal.} \end{aligned} \quad (4)$$

Subtracting

$$2 \text{ HCl(aq, } M=2.0852) = 2 \text{ HCl(aq, } M=2.0852); \Delta H_5 = 0 \quad (5)$$

from eq 4, there is obtained

$$\begin{aligned} & 32.1698 \text{ HCl(aq, } M=2.0852) + 25.9089 \text{ HCl(aq, } M=1.9331) = \\ & 32.1698 \text{ HCl(aq, } M=1.9610) + 25.9089 \text{ HCl(aq, } M=2.0852); \\ & \Delta H_6 = \Delta H_4 - \Delta H_5 = \Delta H_1 - \Delta H_2 + 12 \text{ cal.} \end{aligned} \quad (6)$$

Equation 6 is also obtained when eq 8 is subtracted from eq 7

$$32.1698 \text{ HCl(aq, } M=2.0852) = 32.1698 \text{ HCl(aq, } M=1.9610); \Delta H_7 \quad (7)$$

$$25.9089 \text{ HCl(aq, } M=2.0852) = 25.9089 \text{ HCl(aq, } M=1.9331); \Delta H_8 \quad (8)$$

Therefore,

$$\Delta H_6 = \Delta H_7 - \Delta H_8 = \Delta H_1 - \Delta H_2 + 12 \text{ cal} \quad (9)$$

and

$$\Delta H_1 - \Delta H_2 = \Delta H_7 - \Delta H_8 - 12 \text{ cal.} \quad (10)$$

From table 5 it may be seen that eq 7 and 8 represent the reactions for the dilution of the acid solutions in determinations B and D , respectively. Since account has already been taken of the -12 cal in eq 10 in correcting for the variation of the concentration of MgCl_2 in the final solutions (see table 3) the only remaining correction to be made for differences in concentration is $\Delta H_7 - \Delta H_8$, which, as can be seen from table 5, is equal to $-879 - (-867)$ or -12 cal.

Since the concentrations of all determinations were corrected to those of determination B , the corrections for differences in the concentration of HCl in the final solutions were obtained by subtracting each of the numbers in the last column of table 5 from -879 cal.

These corrections are shown in the third column of table 4.

(b) CORRECTION TO A TEMPERATURE OF 25° C

As it was desired to know the heats of the reactions at 25° C, corrections were made for the departure of the final temperatures from 25° C.

In calculating the temperature coefficient of the reaction, $\text{MgO}(c) + 2 \text{HCl}(aq) = \text{MgCl}_2(aq) + \text{H}_2\text{O}(liq)$, in which the concentrations of the HCl and MgCl_2 solutions were approximately 2 and 0.06 *M*, respectively, the apparent molal heat capacity (at 25° C) of 2 HCl was taken as $-45 \text{ cal/}^\circ\text{C}$ [7] and that of MgCl_2 as $-48 \text{ cal/}^\circ\text{C}$. The latter was estimated from specific-heat data on aqueous solutions of MgCl_2 [8]. The molal heat capacities of MgO [4] and H_2O were taken as $9.1 \text{ cal/}^\circ\text{C}$ and $18 \text{ cal/}^\circ\text{C}$, respectively, at 25° C. The increase in the heat capacity, ΔC_p , resulting from the above reaction is, therefore, $(-48 + 18) - (9.1 + (-45))$, or approximately $+6 \text{ cal}$.

Since

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

and

$$\Delta H_1 = -\Delta C_p (T_2 - T_1) + \Delta H_2,$$

the temperature coefficient of the reaction in question is $-6 \text{ cal/}^\circ\text{C}$. To obtain the temperature corrections it is only necessary then to subtract 25° C from the final temperature of each determination and multiply each result by -6 cal . These corrections are shown in the fourth column of table 4.

V. HEAT OF SOLUTION OF $\text{Mg}(\text{OH})_2$ IN HYDROCHLORIC ACID

Determinations were made of the heat of solution (in 2.085 *M* HCl) of brucite and of $\text{Mg}(\text{OH})_2$ prepared by hydrating MgO for 2 hours at 120 lb/in.² steam pressure (see section III). Data relative to these determinations are shown in table 6. The method by which the corrected heats of solution were obtained was explained in detail in section IV of this paper.

TABLE 6.—Heat of solution of $\text{Mg}(\text{OH})_2$ in 2.085 *M* HCl

[Heat capacity of calorimeter containing 640 g of 2.085 *M* HCl equals $648.3 \pm 0.2 \text{ cal}$.]

Sample	Experiment	Uncorrected heat of solution		Corrected heat of solution of $\text{Mg}(\text{OH})_2$ (c) $+17,630 \text{ g } 2.085 \text{ M HCl} - \text{H}_2\text{O}(\text{liq}) = \text{solution } \Delta H_{248.1^\circ\text{K}}$ equals:
		ΔH <i>cal/g of MgO</i>	ΔH <i>cal/mole</i>	
$\text{Mg}(\text{OH})_2$ (brucite).....	1	-661.2	-----	-----
	2	-661.6	-----	-----
	3	-661.4	-----	-----
Average.....		-661.4	-26,672	-26.64 \pm 0.01
$\text{Mg}(\text{OH})_2$ prepared by hydrating MgO for 2 hr at 120-lb/in. ² steam pressure, 177° C.....	1	-666.9	-----	-----
	2	-667.9	-----	-----
	3	-668.2	-----	-----
	4	-667.0	-----	-----
Average.....		-667.5	-26,917	-26.88 \pm 0.02

Table 6 shows that the heat of solution of brucite is appreciably less than that of the $\text{Mg}(\text{OH})_2$ prepared by the hydration of MgO in the autoclave.

VI. HEATS OF SOLUTION OF CaO AND Ca(OH)₂ IN HYDROCHLORIC ACID

The samples of CaO and Ca(OH)₂ used in determinations of heat of solution were described in section III. As is indicated in tables 7 and 8, determinations were made in both 2.085 and 0.277 *M* HCl. The molal concentrations of CaCl₂ in the final solutions represented by the equations in columns 5 of these tables was in both cases 0.0380 *M*.

The effect of ignition temperature on the heat of solution of CaO has not been studied in this laboratory. However, Gautier [9] has reported heat of solution data on CaO (in hydrochloric acid) prepared by igniting CaCO₃ at temperatures ranging from 1,000° to about 2,570° C (fusion temperature of CaO). He concluded that the temperature at which the CaO was prepared did not affect its heat of solution. In view of the effect of the ignition temperature on the heat of solution of MgO, it should be of particular interest to compare the heat of solution of CaO prepared at high temperatures with that prepared by dehydration of Ca(OH)₂ at relatively low temperatures.

TABLE 7.—Heat of solution of CaO and Ca (OH)₂ in 2.085 *M* HCl[Heat capacity of calorimeter containing 640 g of 2.085 *M* HCl equals 648.3 ± 0.2 cal.]

Sample	Experiment	Uncorrected heat of solution		Corrected heat of solution
		ΔH	ΔH	
CaO prepared from CaCO ₃ by igniting for 4 hr. at 1,050° to 1,100° C.	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	<i>cal/g of CaO</i>	<i>cal/mole</i>	$\left. \begin{array}{l} \text{CaO(c)} + 28,000 \text{ g of } 2.085 \text{ M HCl} = \\ \text{solution; } \Delta H_{298.1^\circ \text{K}} \text{ equals:} \end{array} \right\}$
		—833.6	-----	
		—835.2	-----	
	Average.....	-----	—833.8	-----
Ca(OH) ₂ prepared by hydrating CaO for 2 hr. at 120-lb./in. ² steam pressure (177° C.).	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	—834.2	—46, 774	$\left. \begin{array}{l} \text{Ca(OH)}_2 + 28,000 \text{ g of } 2.085 \text{ M HCl} - \\ \text{H}_2\text{O (liq)} = \text{solution; } \Delta H_{298.1^\circ \text{K}} \\ \text{equals:} \end{array} \right\}$
		—556.8	-----	
		—557.9	-----	
	Average.....	-----	—557.6	-----
Average.....	-----	—557.4	—31, 253	—31.23 ± 0.04 kcal.

TABLE 8.—Heat of solution of CaO and Ca (OH)₂ in 0.277 *M* HCl[Heat capacity of calorimeter containing 640 g of 0.277 *M* HCl equals 689.7 ± 0.9 cal.]

Sample	Experiment	Uncorrected heat of solution		Corrected heat of solution
		ΔH	ΔH	
CaO prepared from CaCO ₃ by igniting for 4 hr. at 1,050° to 1,100° C.	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	<i>cal/g of CaO</i>	<i>cal/mole</i>	$\left. \begin{array}{l} \text{CaO(c)} + 27,416 \text{ g of } 0.277 \text{ M HCl} = \\ \text{solution; } \Delta H_{298.1^\circ \text{K}} \text{ equals:} \end{array} \right\}$
		—825.5	-----	
		—824.2	-----	
	Average.....	-----	—825.9	-----
Ca(OH) ₂ prepared by hydrating CaO for 2 hr. at 120-lb./in. ² steam pressure (177° C.).	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	—825.2	—46, 269	$\left. \begin{array}{l} \text{Ca(OH)}_2(\text{c}) + 27,416 \text{ g of } 0.277 \text{ M} \\ \text{HCl} - \text{H}_2\text{O (liq)} = \text{solution; } \Delta H_{298.1^\circ \text{K}} \\ \text{equals:} \end{array} \right\}$
		—547.8	-----	
		—547.2	-----	
	Average.....	-----	—548.5	-----
Average.....	-----	—547.8	—30, 715	—30.70 ± 0.05 kcal.

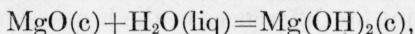
VII. HEATS OF HYDRATION OF MgO AND CaO

The values which have been reported for the heat of hydration of MgO to Mg(OH)₂ differ considerably, as is indicated by table 9. Mixer [10] measured the heat of dehydration of brucite. Roth and Chall [11] state that in their experiments Kahlbaum MgO was used, and that the Mg(OH)₂ was prepared by the slow reaction of water on this MgO, the resulting product being dried to constant weight at 100° C. Giauque and Archibald [4] prepared Mg(OH)₂ by the precipitation method of de Schulten [12]. They state that the crystals of Mg(OH)₂ were well formed, having an average diameter of about 0.2 mm. The MgO was prepared by the dehydration of the precipitated Mg(OH)₂ in vacuo at 300° C.

TABLE 9.—Heat of hydration of MgO to Mg(OH)₂ as reported by various investigators

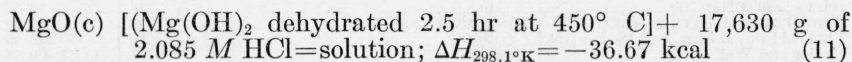
Investigators	Method	Temperature at which determination was made	Heat of hydration, Δ <i>H</i>
		°C	kcal/mole
Mixer [10].....	Reaction of Na ₂ O ₂ with brucite.....		-9.40
Roth and Chall [11].....	Heat of solution.....	50	-8.19
Giauque and Archibald [4].....	do.....	25	-9.74

It can be seen from the data of table 1 that the heat of solution of MgO prepared by dehydrating Mg(OH)₂ at 450° C. was 950 cal per mole greater than that prepared at 1,425° C. Also (table 6) the heat of solution of Mg(OH)₂ prepared by hydrating MgO in the autoclave was 240 cal per mole greater than that of brucite. It should be recalled that Fricke, Schnabel, and Beck [3] have likewise reported differences in the heats of solution of Mg(OH)₂ prepared by various methods. It is apparent then that the heat of hydration of MgO to Mg(OH)₂ may vary considerably, depending on characteristic properties of both the MgO and the Mg(OH)₂ which is formed as the result of the hydration. A heat value for the reaction,

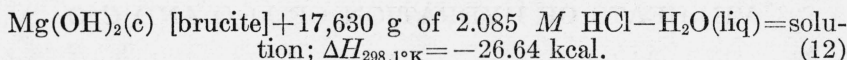


as determined from heat of solution data, is therefore indefinite in meaning unless the samples of MgO and Mg(OH)₂, on which many data have been obtained, are fully described.

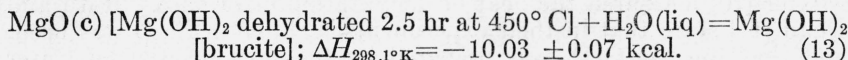
Table 1 shows the equation MgO(c) + 17,630 g of 2.085 *M* HCl = solution; Δ*H*_{298.1°K} = -36.67 kcal, for the solution of MgO prepared by dehydrating Mg(OH)₂(c) for 2.5 hours at 450° C.; table 6, the equation Mg(OH)₂(c) + 17,630 g of 2.085 *M* HCl - H₂O(liq) = solution; Δ*H*_{298.1°K} = -26.64 kcal for the solution of brucite. These equations could be made more definite in their meaning by writing them in the following forms:



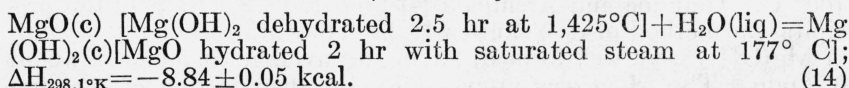
and



By subtracting eq 12 from eq 11, there is obtained



From similar considerations, there may also be written



Still other values for the heat of hydration of MgO can be calculated from the present data, for example: $\text{MgO}(\text{c}) [\text{Mg(OH)}_2 \text{ dehydrated 2.5 hr at } 450^\circ \text{C}] + \text{H}_2\text{O}(\text{liq}) = \text{Mg(OH)}_2(\text{c}) [\text{MgO hydrated 2.5 hr with saturated steam at } 177^\circ \text{C}]; \Delta H_{298.1^\circ\text{K}} = -9.79 \pm 0.07 \text{ kcal.} \quad (15)$

Even though these equations have been made more definite in their meaning by writing in this manner they are still inadequate in that they contain no statement as to the particle size distribution of the materials. There is no assurance that different investigators will obtain end-products having the same particle size. Differences in particle size may give rise to differences in heat effects because of surface phenomena.

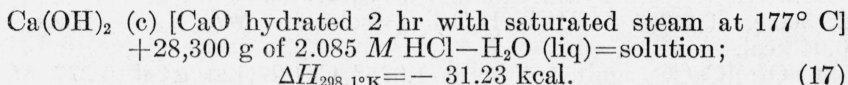
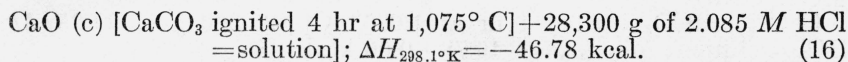
The value -9.79 kcal happens to be very close to $\Delta H_{298.1^\circ\text{K}} = -9.74 \text{ kcal}$ as given by Giauque and Archibald [4] for the heat of hydration of MgO to Mg(OH)_2 computed from their excellent heat-of-solution data. However, inasmuch as their sample of Mg(OH)_2 was composed of crystals having an average diameter of about 0.2 mm, their value should perhaps be compared to -10.03 kcal obtained from eq 13, which pertains to well-developed crystals of brucite, were it not for the fact their MgO was prepared somewhat differently from that given in eq 13. They decomposed their Mg(OH)_2 under vacuum at 300°C , raising the temperature to 350°C toward the end of the decomposition. Apparently, this required 10 days or more of heating. The MgO used in the present investigation was prepared not from brucite but from Mg(OH)_2 obtained with the use of saturated steam. It is believed that differences in the particle size of the samples of MgO largely account for differences in the heats of hydration of MgO to Mg(OH)_2 .

TABLE 10.—Heat of hydration of CaO to Ca(OH)_2 as reported by various investigators

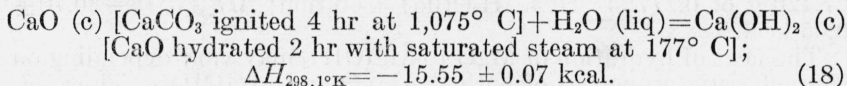
Investigators	Method	Temperature at which the determination was made	Heat of hydration
		$^\circ\text{C}$	kcal/mole
Thomsen [13].....	Heat of solution.....	20	15.54
Berthelot [14].....	Heat of solution and heat of neutralization.....	16	15.10
Roth and Chall [11].....	Heat of solution.....	50	15.44
Thorvaldson, Brown, and Peaker [15].....	do.....	20	15.64
Schwiete and Hey [16].....	do.....	18	15.55
Kohlschutter and Feitknecht [17].....	Direct hydration.....	20	15.30
Thorvaldson, Brown, and Peaker [15].....	do.....	20	15.49
Taylor and Wells.....	Heat of solution.....	25	15.57 ± 0.88
Do.....	Direct hydration.....	25	15.43 ± 0.09

The heat of hydration of CaO to Ca(OH)₂ has been determined by various investigators by differences in the heats of solution of CaO and Ca(OH)₂ in an acid as well as by direct hydration in saturated lime water. The results of these determinations are shown in table 10.

In this investigation the heat of hydration of CaO was determined by both the heat-of-solution and direct method. The heats of solution of CaO and Ca(OH)₂ were each determined in two concentrations of hydrochloric acid (see tables 7 and 8). Modifying the equations in table 7 to describe more definitely the states of the solids, there may be written

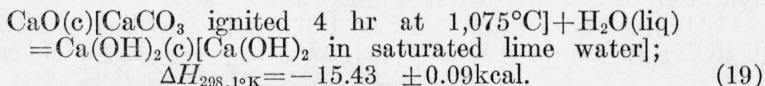


Subtracting eq 17 from eq 16 there is obtained



By a similar treatment of the data for the heat of solution of CaO and Ca(OH)₂ in the more dilute acid, there is obtained for the reaction expressed in eq 18 a value of $\Delta H_{298.1^\circ \text{K}}$ equal to -15.58 ± 0.09 kcal. The average value of $\Delta H_{298.1^\circ \text{K}}$ for this reaction, as determined by the heat-of-solution method, is therefore approximately -15.57 ± 0.08 kcal.

The heat of hydration of CaO to Ca(OH)₂ was also determined by the direct hydration of CaO in saturated lime water. The results of two experiments were -15.38 kcal and -15.47 kcal, or an average of approximately -15.43 ± 0.09 kcal. The reaction of the direct hydration of CaO to Ca(OH)₂ is expressed in the following equation:



VIII. SUMMARY

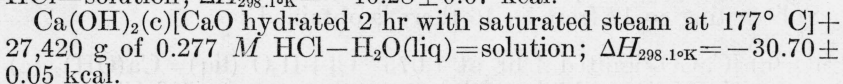
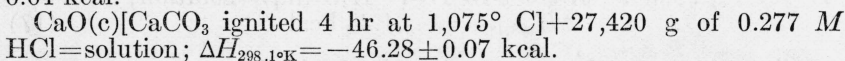
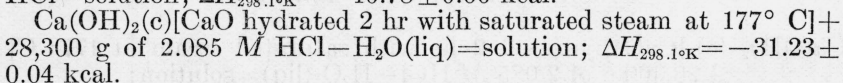
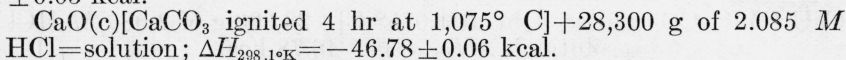
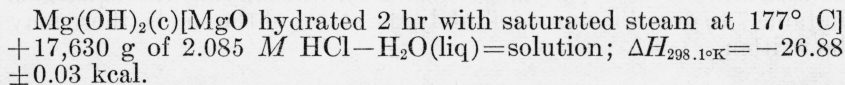
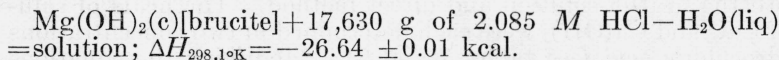
The heat evolved in the solution of MgO in hydrochloric acid was found to decrease as the temperature at which the MgO was prepared was increased. This is shown in the following equations where the values given are those of ΔH , the increment in the heat content. The negative sign, therefore, indicates the evolution of heat.

MgO(c)[Mg(OH)₂ dehydrated 2.5 hr at 450°C] + 17,630 g of 2.085 M HCl = solution; $\Delta H_{298.1^\circ \text{K}} = -36.67 \pm 0.07$ kcal, and MgO(c)[Mg(OH)₂ dehydrated 2.5 hr at 1,425°C] + 17,630 g of 2.085 M HCl = solution; $\Delta H_{298.1^\circ \text{K}} = -35.72 \pm 0.03$ kcal.

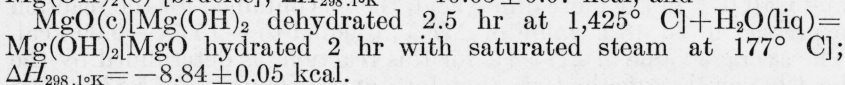
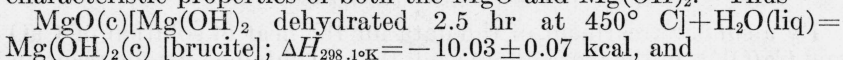
The decrease in the heat evolved has been attributed to an increase in the particle size of the MgO as the temperature of ignition was increased. Since X-ray diffraction patterns were similar there appeared to be no change in crystalline form. The increase in particle

size was indicated by a decrease in the rate of solution in the calorimeter and was verified by sedimentation experiments.

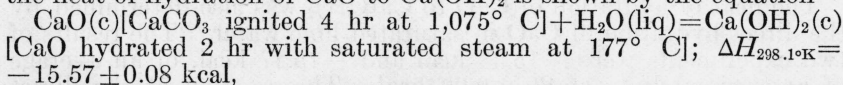
Heat values have also been obtained for the solution of $\text{Mg}(\text{OH})_2$, CaO , and $\text{Ca}(\text{OH})_2$ in hydrochloric acid. The results are summarized in the equations which follow:



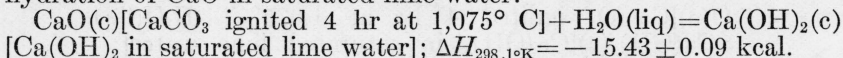
The heat of hydration of MgO to $\text{Mg}(\text{OH})_2$ may vary depending on characteristic properties of both the MgO and $\text{Mg}(\text{OH})_2$. Thus



The result of the determination by the heat-of-solution method of the heat of hydration of CaO to $\text{Ca}(\text{OH})_2$ is shown by the equation



while the following equation shows the result obtained by direct hydration of CaO in saturated lime water:



The authors acknowledge their indebtedness to Frederick D. Rossini for his many helpful suggestions, to Howard F. McMurdie for obtaining the X-ray diffraction patterns, and to Dana L. Bishop for his sedimentation experiments.

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