2. Log l varies linearly with $1/T$ for the organic solvents, but not for water.

3. In the formula $l = ae^{u/RT}$, where u is the heat of solution, it is found that for monatomic molecules, diatomic molecules and for carbon dioxide there is an approximate linear relation between log a and u.

COPENHAGEN, DENMARK

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

STUDIES ON THE THERMOCHEMISTRY OF THE COMPOUNDS OCCURRING IN THE SYSTEM $CaO-Al_2O_3-SiO_2$. II. THE HEAT OF SOLUTION OF CALCIUM HYDROXIDE IN $HCl·200H_2O$[1]

BY THORBERGUR THORVALDSON AND WELDON G. BROWN

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Introduction

Thomsen[2] reports two determinations of the heat of solution of hydrated lime in $HCl·300H_2O$, giving the values 30.41 and 30.57 or a mean of 30.49 kg. calories per mole. The calcium hydroxide is described by Thomsen as a moist powder, 90.88 g. of the material containing 74 g. of $Ca(OH)_2$. Berthelot[3] determined the heat of solution of calcium hydroxide in water and the heat of neutralization of the solution by hydrochloric acid (1 equivalent in 2 liters). He obtained thus the value 30.96 kg. calories per mole for the heat of solution of calcium hydroxide in hydrochloric acid.

An accurate value for the heat of solution of calcium hydroxide in $HCl·200H_2O$ was required in connection with the present studies. Since the two values given above differ by 1.5% and are for different concentrations of acid, it was decided to redetermine the heat of this reaction.

Apparatus and Experimental Procedure

The calorimeter was of the Richards adiabatic type, with a modification in the method of stirring which prevented diffusion or convection of air between the calorimeter and the environment. The stirrer, the Beckmann thermometers and the method of introducing the sample into the calorimeter are described in the first paper of this series.[4]

The air gap between the calorimeter can and the jacket was 6 mm. wide. A negative thermal head[5] of 0.01 ± 0.005° was maintained between the outside jacket and the calorimeter. It was found that fluctuations in

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[1] The authors take pleasure in acknowledging generous financial assistance from the National Research Council of Canada.

[2] Thomsen, "Thermochemische Untersuchungen," **1883**, Vol. 3, p. 248.

[3] Berthelot, *Ann. chim. phys.*, [5] **4**, 531 (1875).

[4] Thorvaldson, Brown and Peaker, THIS JOURNAL, **51**, 2678 (1929).

[5] Thermal head: temperature of calorimeter *minus* temperature of jacket.

the thermal head within these limits did not introduce an appreciable error since the leakage under a negative thermal head of 0.020 ± 0.001°, with a heat capacity of 598 cal./deg., was only 0.001° for thirty-minute intervals. Under a negative thermal head of 0.05° the rise in temperature per ten-minute interval was 0.002° while the corresponding value for a head of 0.10° was 0.0045°. Barry[6] has shown that wider air gaps than the one used in this work decrease the thermal leakage materially for heads of 0.05° and higher; but as the leakage for the thermal head maintained in the determinations described in this paper was negligible, the small air gap was used in preference to a wider one in order to reduce the volume of air in the calorimeter and the uncertain correction for vaporization.

Specific Heats.—The values used in calculating the heat capacity of the calorimeter system were: gold,[7] 0.031; gold alloy (80% Au, 20% Cu)[7] 0.044; $Ca(OH)_2$,[7] 0.27; $HCl{\cdot}200H_2O$[8] (18 to 20°), 0.9826 (20° cal.). All weights were corrected to vacuum.

Purification of Materials

Calcium Carbonate and Calcium Oxalate.—The general procedure used in the preparation of pure calcium oxide is described in the first paper of this series. Similar precautions were taken to assure purity of reagents, thorough washing of precipitates and separation of mother liquors and wash waters. The acids and other reagents were always either freshly redistilled or freshly recrystallized when used.

Sample A.—Calcium carbonate was dissolved in hydrochloric acid, reprecipitated from dilute solution by ammonium carbonate, redissolved in hydrochloric acid and the calcium precipitated as the oxalate by ammonium oxalate.

Sample B.—Calcium nitrate was recrystallized eight times and the calcium precipitated as calcium carbonate. The carbonate was then dissolved in hydrochloric acid and the calcium precipitated from a hot dilute solution as the oxalate.

Sample C.—A very pure sample of calcium nitrate was recrystallized twice in vessels of fused silica and the calcium precipitated as the carbonate.

Sample D.—A very pure sample of recrystallized calcium chloride was treated with excess of bromine and milk of lime, boiled, filtered and changed to the nitrate by repeated evaporation with excess of nitric acid. The solution was filtered and the nitrate was then recrystallized five times in glass and three times in platinum vessels and the calcium precipitated as calcium carbonate (calcite).

Sample E.—Calcium nitrate of high purity was treated with excess of bromine and milk of lime, boiled, filtered, recrystallized twice and the calcium precipitated as calcium carbonate (calcite).

$HCl{\cdot}200H_2O$.—The acid was first redistilled, the condenser tube being fused silica, the middle fraction collected in silica flasks and diluted to $HCl{\cdot}200H_2O$. The adjustment was made by titrations with pure sodium carbonate and by gravimetric determinations of chloride.

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[6] Barry, THIS JOURNAL, **44**, 921 (1922).

[7] "International Critical Tables," **1929**, Vol. V, pp. 92, 120, 99.

[8] Richards, Mair and Hall, THIS JOURNAL, **51**, 727 (1929). This is calculated from the values in mayers for 18 and 20° given in Table I, p. 729. According to a private communication from Dr. Mair, the values given in calories for $HCl{\cdot}200H_2O$ at 18 and 20° are in error.

Saturated Lime-Water.—Excess of pure calcium oxide was shaken with freshly redistilled carbon dioxide-free water. The saturated solution was allowed to stand in contact with excess of calcium hydroxide and was protected from contamination with carbon dioxide.

Preparation of Calcium Hydroxide.—Calcium oxide was prepared from the pure samples of calcium carbonate and calcium oxalate as required, by ignition in platinum crucibles to constant weight in an electric muffle. The oxide was then hydrated in two different ways: by prolonged exposure to water vapor in an evacuated vessel at 21°, or by exposure to saturated steam in an autoclave at 150° for twenty-four hours or more. Precautions were taken to prevent access of carbon dioxide to the material during the preparation. The crucibles were then transferred to a vacuum desiccator over calcium oxide and kept there until constant in weight, when the heat of solution of the material in $HCl \cdot 200H_2O$ was determined. Determinations of the heat of solution of samples hydrated at 21°, containing on the average 13% of water in excess of that required to form $Ca(OH)_2$, were also made. The results are recorded in Tables I, II and III.

It was found that the calcium oxide placed over water in an evacuated vessel absorbed water vapor very rapidly until it had taken up 11 to 15% in excess of the amount required to form calcium hydroxide. All except the last few tenths of a per cent. of this excess of water was removed when the crucible was placed in vacuum over calcium oxide. This last portion of water was held very firmly and was not removed from the samples used for determining the heat of solution. The material prepared in steam at 150° differed in this respect and was almost of the theoretical composition after drying over calcium oxide. When samples of calcium hydroxide, prepared by the two methods and dried to constant weight over lime, were exposed over a saturated solution of ammonium sulfate at 21° (aqueous tension about 15 mm.) the hydroxide which had been prepared at room temperature took up from 3 to 8 times as much water during twenty-four hours of exposure as samples hydrated in steam at 150°.

Microscopic examination of the samples of calcium oxide and of the calcium hydroxide prepared from it by the two methods indicated marked physical differences. The particles of calcium oxide retained the shape and the size of the calcite crystals from which they were formed by ignition. They were weakly birefringent. Hydration by exposure of the ignited calcite to water vapor at 21° still left the shape and size of particles unchanged. The hydrated material had a refractive index[9] of 1.573 ± 0.002 and appeared very weakly birefringent when the sensitive tint plate was used.

The samples prepared by hydration of the ignited calcite in steam at 150° were composed of plates and prisms which were anisotropic and had the indices of refraction given by Ashton and Wilson.[10]

It seems probable that the particles of the calcium hydroxide prepared at 21° have a very large internal as well as external surface and that this is the reason for the large capacity of the material for taking up water vapor.

The literature contains some evidence for the formation of a dihydrate of calcium oxide below 60°. Haslam, Calingaert and Taylor[11] attempted

[9] Measurements by V. A. Vigfusson.

[10] Ashton and Wilson, *Am. J. Sci.*, **13**, 218 (1927).

[11] Haslam, Calingaert and Taylor, THIS JOURNAL, **46**, 308 (1924).

without success to prepare this hydrate and, further, found no evidence for its existence from their study of the solubility curve for calcium hydroxide. The relative values obtained for the heat of solution of calcium hydroxide as given in Tables I, II and III do not indicate the formation of a higher hydrate when calcium hydroxide takes up water vapor at 21°.

TABLE I

HEAT OF SOLUTION OF CALCIUM HYDROXIDE, PREPARED BY EXPOSURE OF CaO TO WATER VAPOR AT 21° WITH SUBSEQUENT DRYING OVER CaO, IN $HCl \cdot 200H_2O$

Sample	CaO, g.	H_2O taken up, %	H_2O excess, %	Final temp., °C.	Corr. rise, °C.	Heat of soln. per gram of CaO, cal.$_{20°}$
B	2.2468	32.73	0.60	19.87	2.080	553.8
C	1.9967	32.49	.36	20.04	1.850	554.2
C	2.2470	32.50	.37	20.05	2.083	554.6
C	2.2304	32.54	.41	20.04	2.069	554.9
C	2.2506	32.44	.31	19.96	2.083	553.7
C	2.2293	32.53	.40	19.98	2.061	553.0
C	2.2257	32.34	.21	20.04	2.058	553.1
D	2.2200	32.74	.61	20.01	2.056	554.0
D	2.2099	32.72	.59	20.00	2.045	553.6
Mean		32.56	.43	20.00		553.8

TABLE II

HEAT OF SOLUTION OF CALCIUM HYDROXIDE, PREPARED BY EXPOSURE OF CaO TO SATURATED STEAM AT 150° WITH SUBSEQUENT DRYING OVER CaO, IN $HCl \cdot 200H_2O$

Sample	CaO, g.	H_2O, taken up, %	H_2O excess, %	Final temp., °C.	Corr. rise, °C.	Heat of soln. per gram of CaO, cal.$_{20°}$
A	1.9055	32.19	0.06	20.03	1.754	550.7
C	2.4333	32.02	− .11	20.17	2.242	551.1
C	2.2345	32.07	− .06	19.99	2.057	550.7
C	2.1603	32.08	− .05	19.97	1.989	550.5
C	2.1969	32.11	− .02	19.98	2.023	550.9
D	2.2268	32.08	− .06	20.01	2.053	551.5
D	2.2399	32.04	− .09	20.06	2.061	550.4
Mean		32.08	− .05	20.03		550.8

TABLE III

HEAT OF SOLUTION OF CALCIUM HYDROXIDE, PREPARED BY EXPOSURE OF CaO TO WATER VAPOR AT 21°, CONTAINING A LARGE EXCESS OF WATER

Sample	CaO, g.	H_2O taken up, %	H_2O excess, %	Final temp., °C.	Corr. rise, °C.	Heat of soln. per gram of CaO, cal.$_{20°}$
D	2.2179	43.30	11.17	20.09	2.043	551.0
E	2.2425	47.98	15.85	19.99	2.064	550.6
E	2.2185	44.96	12.83	19.99	2.039	549.8
E	2.2333	44.96	12.83	20.04	2.057	551.0
E	2.2314	44.80	12.67	20.04	2.053	550.4
Mean		45.20	13.07	20.03		550.6

NOTES ON TABLES I, II AND III

(a) The weight of $HCl{\cdot}200H_2O$ used in each experiment was 600.4 g. The water equivalent of the apparatus was 8.2 cal./deg., and the total heat capacity 598.2 $cal._{20°}$.

(b) The figures in the column headed "corr. rise" were corrected for (1) stirring, (2) stem exposed, (3) setting of thermometer and (4) variation in the temperature of the sample of calcium hydroxide from 20° at the time of introduction into the calorimeter.

Discussion of the Experimental Results

One small correction should be applied to the values obtained in Tables I, II and III. The air in the calorimeter system, which amounted to about 600 cc., was no doubt saturated with water vapor (at the tension of $HCl{\cdot}200H_2O$ at 18°) at the beginning and practically saturated at 20° at the end of each experiment. The calculated amount of heat absorbed by evaporation is 0.18 calorie per gram of CaO. Applying this correction, the isothermal heats of solution of the three samples of calcium hydroxide in $HCl{\cdot}200H_2O$ at 20.0° become 554.0, 551.0 and 550.8 $cal._{20°}$ per gram of CaO, or 31.06, 30.89 and 30.88 kg. $cal._{20°}$ per mole, respectively.

Thus the value obtained for the heat of solution of the calcium oxide hydrated at room temperature is 3 calories per gram higher than that obtained with the material hydrated in steam at 150°. This difference is much in excess of the probable experimental error of the determinations. Further, the material which contained on the average 0.43% of water in excess of the theoretical amount (Table I) gives a higher heat of solution than the samples which contained within 5 parts in 13,000 of the theoretical quantity of water of hydration for $Ca(OH)_2$.

The optical examination suggests that the calcium hydroxide prepared at room temperature may not be crystalline and that the two may differ in the energy of crystal lattice. The difference in the rate of adsorption of water vapor by the samples prepared by the two different methods suggests that they may differ in surface energy. Either of these, or both combined, might be the cause of the difference in the value for the heat of solution.

Photographs of the x-ray diffraction pattern of samples of calcium hydroxide prepared by both these methods were made. In each case the same diffraction pattern was obtained and this was identical with that given by Harrington.[12] The results cannot be considered to exclude entirely the possibility of differences in lattice energy at the time of the determination of the heat of solution, as in each case some time elapsed between the preparation of the sample and the making of the x-ray photograph. The samples, however, appeared unchanged when the photographs were taken.

The fact that the particles of the calcium hydroxide prepared at room temperature retained the shape and size of the calcite crystals from which they were prepared and, therefore, probably possessed internal surface,

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[12] Harrington, *Am. J. Sci.*, [5] 13, 467 (1927).

excluded the possibility of making an estimate of the relative effective surface area of the samples. An approximate measure of the surface energy of the material can, however, be obtained by determining its heat of adsorption or its heat of wetting. From Tables I and III it appears that when calcium hydroxide of the composition CaO + 32.56% of H_2O prepared at room temperature adsorbs an additional 12.6% of water vapor, 3.2 calories per gram of CaO are given out. To obtain further evidence as to differences in surface energy, the heat of wetting of samples of calcium hydroxide prepared by each of the methods was determined.

Determinations of the Heat of Wetting of Calcium Hydroxide.—The same calorimeter was used as for the determination of the heat of solution. The sample of calcium hydroxide was introduced in the usual way after the calorimeter, containing saturated lime-water, had come to thermal equilibrium at 20°. The results are given in Tables IV, V and VI.

Table IV

Heat of Wetting of Calcium Hydroxide, Prepared by Exposure of CaO to Water Vapor at 21° with Subsequent Drying over CaO, by Saturated Lime-water

Total heat capacity, 607 cal./deg.

Expt.	CaO, g.	H_2O, %	Temp. rise, 1st sample, °C.	Temp rise, other samples, °C.	Heat of wetting, cal. per g. of CaO
1A[a]	3.87	32.66	0.030		
1B	3.85	32.69		0.025	3.9
2A	3.93	32.63	.026		
2B	3.92	32.61		.021	3.3
3A	3.88	32.64	.026		
3B	3.85	32.68		.021	3.3
3C	3.87	32.65		.020	3.1
3D	3.87	32.64		.019	3.0
4	3.88	32.70	.026		3.0[b]
5	3.81	32.60	.029		3.5[b]
		32.65			3.3

[a] Each of the groups 1A and B, 2A and B, etc., represent successive runs without changing the lime-water in the calorimeter. The temperature rise for the first run of each group given in the fourth column is, in each case, a few thousandths of a degree higher than for the remaining runs in the group. This was shown, both by titration with acid and by measurement of electrical conductivity of the lime-water in the calorimeter before and after an experiment, to be due to supersaturation. The conductivity electrodes were mounted within the calorimeter and in this way it was found that the supersaturation reached a maximum in less than one minute after the first sample of calcium hydroxide was introduced and that it did not change with the addition of further samples.

[b] In Experiments 4 and 5 the supersaturation was found to be 12.7 and 12.1%, respectively. A correction was made for this supersaturation, using 50 cal. per gram of CaO as the heat of solution of calcium hydroxide in water, in calculating the heat of wetting.

The occurrence of supersaturation under these conditions is of special interest since Goldammer[13] has reported that although calcium oxide is capable of forming supersaturated solutions, calcium hydroxide is not.

TABLE V

HEAT OF WETTING OF CALCIUM HYDROXIDE, PREPARED BY EXPOSURE OF CaO IN STEAM AT 150° WITH SUBSEQUENT DRYING OVER CaO IN SATURATED LIME-WATER

Expt.	CaO, g.	H_2O, %	Heat cap., cal./deg.	Temp. rise, °C.	Heat of wetting, cal. per gram of CaO
1A	3.85	32.10	607	0.007	1.1
1B	3.85	32.08	607	.007	1.1
2A	2.2	32.11	607	.003	0.8
2B	2.2	32.17	607	.003	0.8
3A	3.96	32.15	507	.007	0.9
3B	3.95	32.19	507	.009	1.2
	Mean	32.13			1.0

No supersaturation was produced with the material hydrated in steam at 150°.

TABLE VI

HEAT OF WETTING OF CALCIUM HYDROXIDE, PREPARED BY EXPOSURE OF CaO TO WATER VAPOR AT 21° AND CONTAINING A LARGE EXCESS OF H_2O IN SATURATED LIME-WATER

Total heat capacity, 607 cal./deg.

Expt.	CaO, g.	H_2O, %	Temp. rise, °C.	Supersaturation		Heat of wetting, cal. per g. of CaO
				%	Temp. rise, °C.	
1B[a]	3.94	43.3	0.003			0.5
1C	3.95	43.7	.002			.3
2A	3.98	42.0	.007	7.8	0.005	.3
2B	4.08	42.4	.004			.6
3A	3.70	47.1	.009	8.0	.005	.7
3B	4.01	48.1	.004			.6
	Mean	44.4				0.5

[a] Each of the experiments in the same group (A, B, etc.), represents successive runs without changing the lime-water in the calorimeter. The temperature rise for the initial "A" runs is in each case a few thousandths of a degree higher than for the remaining runs (B, C) on account of supersaturation. The supersaturation as determined by titration is given in the fifth column and the rise in temperature, calculated for the supersaturation found, is given in the sixth column.

The values obtained for the heat of wetting of the various samples of calcium hydroxide indicate that difference in surface energy is at least mainly responsible for the variation in the values obtained for the heat of solution. If we subtract in each case the value obtained for the heat of wetting from the value for the heat of solution of calcium hydroxide prepared by the same method, we obtain the following results.

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[13] Goldammer, *Pharm. Centr.*, **26**, 442 (1890).

Prepared by hydration	Cal. per g. of CaO
In steam at 150°	550.0
In water vapor at 21° (13% excess of water)	550.3
In water vapor at 21° (0.43% excess of water)	550.7

These values are in good agreement. While subtracting the heat of wetting does not necessarily eliminate entirely the factor of surface energy, as the material having the larger specific surface has still greater surface energy at the solid–liquid interface, yet this difference is probably small as compared with the heat of wetting. One would, therefore, expect that 550.0 $cal._{20°}$ per gram of CaO is close to the true value for the isothermal heat of solution of calcium hydroxide, possessing a negligible quantity of surface energy, in $HCl{\cdot}200H_2O$ at 20°; but considering that the three values obtained above agree very nearly within the probable experimental error, it would probably be best to take the mean value 550.3 $cal._{20°}$ per gram of CaO, which corresponds to 30.85 kg. $cal._{20°}$ (129.0 Kj.) per mole of $Ca(OH)_2$.

Summary and Conclusions

1. Calcium hydroxide prepared by three methods gave the following values for the isothermal heat of solution at 20° in $HCl{\cdot}200H_2O$: (a) prepared from CaO in water vapor at 21°, dried over quicklime, 554.0 $cal._{20°}$ per gram of CaO (31.06 kg. $cal._{20°}$ per mole); (b) prepared from CaO in steam at 150°, dried over quicklime, 551.0 $cal._{20°}$ per gram of CaO (30.89 kg. $cal._{20°}$ per mole); (c) prepared as (a) but not dried over quicklime, 550.8 $cal._{20°}$ per gram of CaO (30.88 kg. $cal._{20°}$ per mole).

2. Samples of calcium hydroxide prepared by methods (a) and (b), while appearing very dissimilar under the microscope, gave the same x-ray diffraction pattern.

3. Samples of calcium hydroxide prepared by methods (a) and (c) gave supersaturated solutions when added to saturated lime-water, but samples prepared by method (b) did not behave in this manner.

4. The above three samples had the following average heats of wetting in saturated lime water at 20°: (a) 3.3, (b) 1.0, (c) 0.5 cal. per gram of CaO.

5. Subtracting the heat of wetting in each case from the corresponding heat of solution, one obtains the following values: (a) 550.7, (b) 550.0, (c) 550.3 $cal._{20°}$ per gram. The average value 550.3 $cal._{20°}$ per gram of CaO or 30.85 kg. $cal._{20°}$ (129.0 Kj.) per mole is considered to be the most reliable value for the isothermal heat of solution of calcium hydroxide in $HCl{\cdot}200H_2O$ at 20°.

6. No evidence was found that a hydrate of lime higher than $CaO{\cdot}H_2O$ forms at 21°.

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