iodine replaced by oxygen, 35.91% of the red precipitate; iodine replaced calculated from loss in weight, 35.91% of the red precipitate; atoms of iodine replaced, 5.54. The white substance, though not of definite composition, was obviously formed by the replacement of nearly six of the nine original atoms of iodine by an equivalent of oxygen. The composition, therefore, tends toward the limit expressed by the formula $Bi_2O_3 \cdot 3CsI$, but neither the pure white color nor the sensible constancy in weight is a reliable indication that this limit has been reached.

The use of cesium bismuth iodide in the quantitative determination of cesium is being investigated.

The authors wish to express their appreciation of the interest which Professor H. H. Willard has taken in the progress of this work.

Summary

1. A new method for the preparation of cesium bismuth iodide has been described and the properties of cesium bismuth iodide, which have significance in analysis, have been studied.

2. The very low solubility in ethyl alcohol, the constancy in weight at 210°, and the quantitative reaction with standard potassium iodate have been noted.

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[Contribution from the Chemical Laboratory of the University of Saskatchewan]

STUDIES ON THE THERMOCHEMISTRY OF THE COMPOUNDS OCCURRING IN THE SYSTEM $CaO-Al_2O_3-SiO_2$. III. THE HEAT OF HYDRATION OF CALCIUM OXIDE[1]

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Introduction

Several values for the heat of hydration of calcium oxide are to be found in the literature. Thomsen[2] obtained the value 15,540 calories per mole at 20° from data on the heat of solution of calcium oxide and calcium hydroxide in $HCl \cdot 300H_2O$. Berthelot[3] determined the heat of solution of calcium oxide in hydrochloric acid (one-sixth molal) at 16°, the heat of solution of calcium hydroxide in water and the heat of neutralization of a solution of calcium hydroxide by 0.5 *M* hydrochloric acid. From these results he calculated the heat of hydration of calcium oxide, obtaining the

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[1] The authors wish to acknowledge generous financial assistance from the National Research Council of Canada.

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

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

value 15,100 calories per mole. Kohlschütter and Feitknecht[4] obtained the value 15,300 calories per mole at 20° by measuring directly the heat of hydration of calcium oxide in boiled water using a Dewar flask as a calorimeter. Roth and Chall,[5] using a calorimeter with a reaction vessel of porcelain designed for work at higher temperatures, obtained 15,440 calories per mole at 50° from determinations of the heats of solution of calcium oxide and calcium hydroxide in $HCl \cdot 24.65H_2O$ at this temperature. Calculating the temperature coefficient of the reaction from the difference in the heat capacities of the factors and products (7.65 calories per mole per degree between 20 and 50°) and applying this correction, one obtains 15,210 calories per mole at 20°. These authors also quote a determination by Drägert which gave the value 15,175 calories per mole at 15°.

The value obtained by the direct hydration of calcium oxide in water is probably affected slightly by the heat of solution of calcium hydroxide in the water. It should further be noted that values for the heat of hydration obtained by the direct and the indirect methods are not directly comparable. The result obtained by the former method may be considered to include the heat of wetting of the resulting calcium hydroxide in lime water. When the latter method is used, the heat of solution of the calcium hydroxide, which includes the total surface energy of the material, is subtracted from the heat of solution of calcium oxide. One would, therefore, expect the value obtained by the indirect method to be lower than the value obtained by the direct method, the difference being equal to the heat of wetting of the calcium hydroxide. Variations in the heat of wetting[6] of different samples of calcium hydroxide indicate that the value for the surface energy may vary considerably according to the method of preparation. The effect of such factors as these has not been considered in previous determinations of the heat of hydration of calcium oxide.

The surface energy of the calcium oxide appears in the value for the heat of hydration determined by either method. It is possible that this may also vary, although the constancy of the heat of solution of calcium oxide prepared from calcite by ignition at different temperatures[7] and the close agreement between the values for the heat of solution of calcium oxide prepared from calcium oxalate, calcite and aragonite[7] indicates fair constancy for calcium oxide prepared by the methods in common use.

Apparatus and Experimental Procedure.—The calorimeter, which was of the Richards adiabatic type with a slight modification, the Beckmann thermometers, the method of introducing the sample into the calorimeter and the limits of adiabatic control have been described in the first and

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[4] Kohlschütter and Feitknecht, *Helv. Chim. Acta*, **6**, 359 (1923).

[5] Roth and Chall, *Z. Elektrochem.*, **34**, 185 (1928).

[6] Thorvaldson and Brown, THIS JOURNAL, **52**, 80 (1930).

[7] Thorvaldson, Brown and Peaker, *ibid.*, **51**, 2678 (1929).

second papers of this series.[6,7] A copper calorimeter vessel lined with gold was used for these determinations, the hydrating liquid being saturated lime water in order to avoid the thermal effect due to solution of lime.

Specific Heats.—The values used in calculating the heat capacity of the calorimeter system were: copper,[8] 0.092; gold,[8] 0.031; gold alloy (80% Au, 20% Cu),[8] 0.044; CaO,[8] 0.19. All weights were corrected to vacuum.

The specific heat of saturated lime water over the temperature interval 18–20° was determined by the method of Richards and Rowe.[9] Four determinations gave the values 0.9980, 0.9971, 0.9979 and 0.9987, or a mean of 0.9979. The value 0.998 was used in the calculations.

Purification of Materials

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.

Calcium Oxide.—The procedure used for the preparation of pure calcium oxide and the precautions taken to assure purity of reagents were described in the first paper of this series.[7]

Samples A and B.—Commercial "precipitated" calcium carbonate was dissolved in freshly redistilled nitric acid. The neutral solution was treated with excess of bromine and milk of lime, boiled, filtered and the calcium nitrate recrystallized four times. Sample A was prepared by precipitating the calcium as oxalate from a dilute solution of the nitrate with recrystallized ammonium oxalate. Sample B was prepared by a double precipitation as calcium carbonate (calcite) with redistilled ammonium carbonate.

Sample C.—This was prepared from a very pure sample of recrystallized calcium chloride by precipitation as calcium carbonate (calcite) from a 1% solution of the chloride with freshly redistilled ammonium carbonate.

Sample D.—Calcium nitrate was recrystallized eight times and the calcium then precipitated as calcium carbonate (calcite).

Calcium oxide was prepared from these samples as required by ignition to constant weight in platinum in a muffle furnace.

Determination of the Heat of Hydration of CaO.—Of some twenty samples of pure calcium oxide prepared, only five were found to hydrate completely in the calorimeter within one hour. Samples prepared from minutely crystalline calcium carbonate (calcite) or from samples containing an appreciable amount of the spherulitic form, had a tendency to cake slightly on ignition and were found to hydrate more slowly than samples prepared from more coarsely crystalline calcite which generally did not cake. In the case of the more coarsely crystalline materials, the rate of hydration could in some cases be increased by grinding the sample before ignition, but prolonged grinding resulted in caking on ignition and consequently in a slower rate of hydration.

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[8] "International Critical Tables," **1929**, Vol. V, pp. 88, 91, 92, 120.

[9] Richards and Rowe, *Proc. Am. Acad.*, **49**, 191 (1913).

Table I

Direct Determination of the Heat of Hydration of Calcium Oxide

"Water equivalent" of apparatus	18.47 cal./deg.
500.3 g. saturated lime water	499.3 cal./deg.
Total heat capacity—Expts. 1–8	517.8 cal./deg.
Total heat capacity—Expts. 9–11	517.2[a] cal./deg.

Expt.	Sample of CaO	CaO, g.	Final temp., °C.	Time, min.	Temp. rise,[b] °C.	Heat of hydration, 20° cal. per g. of CaO
1	A	3.9829	19.98	20	2.127	276.5
2	A	3.9372	20.27	16	2.100	276.2
3	B	3.8993	20.24	40	2.085	276.9
4	B	3.9853	20.24	36	2.133	277.1
5	C	3.8798	19.81	42	2.066	275.7
6	C	3.7524	19.93	48	1.999	275.9
7	C	3.6393	20.08	32	1.938	275.7
8	C	3.7004	19.95	14	1.973	276.0
9	D	3.7517	20.03	16	2.007	276.7
10	D	3.7982	20.07	14	2.046	278.6
11	D	3.6391	20.10	16	1.416	277.5
Average			20.06°			276.6
Corrected for evaporation						276.8

[a] In Expts. 9, 10 and 11 a different Beckmann thermometer with a 0.6 cal./deg. lower water equivalent was used. [b] These values are corrected for (1) stirring, (2) stem exposed, (3) setting of thermometer and (4) variation in temperature of CaO from 20° at time of introduction into the calorimeter.

As the solubility of calcium hydroxide decreases with rising temperature, one might expect this substance to separate out with absorption of heat during the determination of the heat of hydration. It was, however, found that some calcium oxide dissolves, producing a supersaturated solution. This is in agreement with the observation of Miller and Witt,[10] who found that when calcium oxide is shaken with water in excess of the amount required to form the hydroxide, a supersaturated solution results, the maximum concentration being reached in about four hours, after which it diminishes very gradually, a saturated solution not being obtained until after shaking for more than twenty-four hours.

The amount of supersaturation varied with different samples of calcium oxide. With a sample which hydrated slowly, the supersaturation one-half hour after the introduction of the sample of CaO was found by titration to be 3%, while with three samples which hydrated quickly (in about ten minutes) it was found to be 10.6, 11.0 and 11.7%, respectively. Determination of the supersaturation by the conductivity method gave a somewhat lower value. Both this and the marked tendency of the particles of lime to pass through the filter paper suggests that a part of the supersaturation as determined by titration may have been due to colloid

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[10] Miller and Witt, *J. Phys. Chem.*, **33**, 285 (1929).

particles of calcium hydroxide. From the average value of the determinations of supersaturation made, it appears that a correction of 0.5 cal. per gram of CaO should be applied to the value in Table I as a correction for heat of solution.

Applying this correction, the value for the isothermal heat of hydration of calcium oxide at 20° becomes 276.3 $\text{cal.}_{20°}$ per gram or 15.49 kg. $\text{cal.}_{20°}$ (64.76 kj.) per mole.

Calculation of the Heat of Hydration of CaO from the Heats of Solution of CaO and $Ca(OH)_2$ in $HCl{\cdot}200H_2O$.—The heat of solution of calcium oxide in $HCl{\cdot}200H_2O$ at 20° was found to be 829.2 $\text{cal.}_{20°}$ per gram,[7] and the corresponding value for calcium hydroxide, less the heat of wetting of the hydroxide in saturated lime water, was found to be 550.3 $\text{cal.}_{20°}$ per gram of CaO.[6] Subtracting the second value from the first gives the figure 278.9 $\text{cal.}_{20°}$ per gram for the heat of hydration of calcium oxide at 20°. This figure is 2.6 cal. per gram in excess of the value obtained above by direct hydration of CaO in saturated lime water.

In searching for the cause of this discrepancy one observes that the ratio of calcium oxide to hydrochloric acid used in the determinations of the heat of solution of calcium hydroxide was lower than that used in the determination of the heat of solution of calcium oxide. Determinations were, therefore, made of the heat effect produced on mixing $HCl{\cdot}200H_2O$ with the final solution obtained in determining the heat of solution of calcium oxide in $HCl{\cdot}200H_2O$.[7] No heat effect was observed, so that no error had been introduced from this source.

Microscopic examination of the calcium oxide and calcium hydroxide suggested a possible explanation of the discrepancy. It was found that the particles of calcium oxide retained the shape and the size of the original calcite crystals from which they were made. During hydration and for some time after the temperature of the calorimeter reached apparent constancy, physical changes occurred, the rate of these changes varying with different samples of calcium oxide. In the case of samples hydrating rapidly, the particles broke up into very small fragments during the hydration; in other cases this process was very slow, gradual accumulation of minute globules in the liquid and on the surface of the large particles being observed. M. v. Glasenapp[11] describes the production of colloidal hydrated lime by exposing a material containing free CaO to water. The "droplets" shown in the photographs published by v. Glasenapp, some free in the liquid and others attached to the larger aggregates, appear to be similar to the small rounded particles described above.

It is possible that during the first step of the hydration of calcium oxide in lime water, colloidal calcium hydroxide is formed and the calorimetric measurements give the heat effect for this reaction. The very slow changes

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[11] M. v. Glasenapp, *Kolloid-Z.*, **31**, 195 (1922).

in the physical condition of the particles which continue for a long time may be accompanied by the evolution of appreciable quantities of heat, thus explaining the low value obtained in measuring directly the heat of hydration.

Summary and Conclusions

1. The value 276.3 $cal._{20°}$ per gram or 15.49 kg. $cal._{20°}$ (64.76 kj.) per mole was obtained for the heat of hydration of CaO in saturated lime water at 20°.
2. This value is 2.6 cal. per gram lower than the value (278.9 $cal._{20°}$ per gram, 15.64 kg. $cal._{20°}$ per mole) obtained by calculation from the heats of solution of calcium oxide and calcium hydroxide in $HCl \cdot 200H_2O$.
3. Microscopic examination indicated that physical changes in the hydrated material continue for a long time after the temperature of the calorimeter comes to apparent constancy. It is suggested that changes in the energy of surface and of crystal lattice may be responsible for the discrepancy between the observed and calculated results for the heat of hydration of calcium oxide.

SASKATOON, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

IONIC RATIOS IN THE WATERS OF THE NORTH PACIFIC OCEAN[1]

BY THOMAS G. THOMPSON AND CALVERT C. WRIGHT

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During the past sixty years a number of papers[2] have appeared giving the analyses of sea water from various regions of the world. From some of these data the ratios of the various ions occurring in the waters of the several oceans may be calculated. Such ratios give valuable information as to the constancy of composition of sea water; and, once established and referred to the chlorinity[3] as unity, may be used to calculate the con-

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[1] Paper read before the Pacific Intersectional meeting of the American Chemical Society held at Berkeley, California, June 21, 1929.

[2] (a) Thorpe and Morton, *Ann.*, **158**, 122 (1871); (b) Dittmar, "Reports of H. M. S. "Challenger," *Phys. and Chem.*, **1884**, Vol. 1; (c) Schmidt, *Bull. Acad. St. Petersburg*, **24**, 231 (1878); (d) Schmelck, "Den Norske Nordhavs-Exped.," Part 9, **1882**, p. 1; (e) Forsberg, "Vega Exped. Rept.," **1883**, Vol. 2, p. 376; (f) Kolotoff, *J. Russ. Phys.-Chem. Soc.*, **24**, 82 (1893); (g) Makin, *Chem. News*, **77**, 155 (1898); (h) Natterer, *Monatsh.*, **13**, 873 (1892); **14**, 624 (1893); **15**, 530 (1894); **16**, 405 (1895); **20**, 1 (1899); **21**, 1037 (1900); (i) Schloesing, *Compt. rend.*, **142**, 320 (1906); (j) Coppock, *Chem. News*, **96**, 212 (1907); (k) Wheeler, THIS JOURNAL, **32**, 646 (1910); (l) Bertrand, *Compt. rend.*, **174**, 1251 (1922).

[3] The chlorinity of sea water is defined as the number of grams of chloride ions contained in a kilogram of water, assuming that the small amounts of bromide ions and traces of iodide ions have been converted to chlorides.