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

STUDIES ON THE THERMOCHEMISTRY OF THE COMPOUNDS OCCURRING IN THE SYSTEM $CaO–Al_2O_3–SiO_2$. I. THE HEAT OF SOLUTION OF CALCIUM OXIDE IN HYDROCHLORIC ACID[1]

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The immediate reason for undertaking the work described in this paper was that a reliable value for the heat of solution of calcium oxide in hydrochloric acid was required for the calculation of the heats of formation of the calcium aluminates from the heats of solution of these substances. The values obtained by Berthelot[3] and Thomsen[4] were 46.06 and 46.03 calories per mole of CaO, respectively. From three determinations (46.03, 46.14 and 46.33), Bäckström[5] arrived at the weighted mean 46.20 calories (24°) per mole for the heat of solution of calcium oxide in normal hydrochloric acid at 25°. For our calculations a value for the heat of solution in more dilute acid was required.

Apparatus

The calorimeter used was of the adiabatic type developed by Richards[6] and his collaborators with certain slight modifications. A gold calorimeter vessel was used and the stirring of the liquid in the calorimeter vessel was effected by a motor-driven rotary stirrer made of an alloy of 80% of gold and 20% of copper. The stirrer was insulated from its shaft by a rod of hard rubber. The shaft made an air-tight joint where it passed through the brass tube in the cover of the calorimeter jacket so that diffusion of air between the calorimeter and the environment was eliminated. The rate of stirring was controlled by an external resistance so as to be constant as shown by a revolution counter attached to the shaft of the stirrer. A rate of 290 revolutions per minute was found to be sufficient to prevent thermal stratification in the calorimeter. This rate gave a rise of temperature of 0.001° per minute.

Two series of determinations of the thermal leakage of the calorimeter under a thermal head of 0.010 ± 0.001° and 0.020 ± 0.001°, respectively, were made. After the system was in equilibrium (water equivalent, 600 cal.) the calorimeter stirrer was stopped for ten-minute intervals and then started again. In each case the rise in temperature due to thermal leakage during the ten-minute interval was less than 0.0005°.

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[2] This paper represents part of the theses presented by W. G. Brown and C. R. Peaker in partial fulfilment of the requirements for the degree of M.Sc. in Chemistry at the University of Saskatchewan.

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

[4] Thomsen, "Thermochemische Untersuchungen," **1883**, Vol. 3, p. 247.

[5] Bäckström, THIS JOURNAL, **47**, 2443 (1925).

[6] (a) Richards, Henderson and Forbes, *Proc. Am. Acad.*, **41**, 3 (1905); (b) Richards, Rowe and Burgess, THIS JOURNAL, **32**, 1176 (1910).

The Beckmann thermometers employed had been calibrated at the U. S. Bureau of Standards. A careful comparison with a Beckmann thermometer which had been calibrated by one of us by a thermochemical method[7] gave an agreement within 0.001° over the whole range of the thermometer scale. The actual centigrade temperatures were obtained by comparison with a calibrated standard, the ice-point being taken at the same time.

The large discrepancies often found between thermochemical results from different laboratories indicate the importance of the elimination of constant errors. It was therefore considered advisable to carry out some measurements of well-known thermochemical constants, with this apparatus, before proceeding with the determination of the heat of solution of calcium oxide. Two determinations were chosen: the first involving a temperature rise of 4°, *i. e.*, the neutralization of sulfuric acid using special vessels and solutions identical with those used by Richards and Rowe;[8] the second involving a very small rise of temperature (about 0.15°) *i. e.*, the heat of dilution of $HCl \cdot 20H_2O$ to $HCl \cdot 200H_2O$ according to the method of Richards, Rowe and Burgess.[6b] In both cases the method of stirring described above was used.

A series of six determinations of the heat of neutralization of sulfuric acid gave the values 16,979, 16,997, 16,990, 16,972, 16,982 and 16,984 or a mean of 16,984 calories per $^1/_2$ H_2SO_4 at 20° as compared with 16,982 calories given by Richards and Rowe.[8] Ten determinations of the heat of dilution of $HCl \cdot 20H_2O$ to $HCl \cdot 200H_2O$ gave a mean value of 552 calories per mole, the highest value being 556 and the lowest 549, as compared with 556 calories obtained by Richards, Rowe and Burgess,[6b] 549 calories reported by Richards and Rowe[9] and 552 calories calculated from dilution results by Richards and Thorvaldson.[10] The agreement between the results is all that could be expected and indicates an absence of constant errors affecting the temperature measurements.

Materials

Hydrochloric Acid.—The purest acid of commerce was diluted and redistilled with a quartz condenser, the middle portion of the distillate being collected in quartz flasks. This was then diluted with water freshly redistilled with a block tin condenser and adjusted to $HCl \cdot 200H_2O$, the concentration being checked both by titration with pure sodium carbonate and by gravimetric determinations of chloride.

Calcium Oxide.—The procedure used for eliminating impurities from the calcium salts was essentially similar to that recommended by Richards and Hönigschmid.[11]

The water and the reagents used, such as acids, ammonia, ammonium carbonate and ammonium oxalate, were all purified by redistillation or recrystallization immediately before use. The calcium salts to be purified were in each case, to begin with, of the highest quality obtainable ("for analysis," "special," "analyzed"). The mother liquors were separated from the recrystallized products by means of high-speed power centrifuges. Precipitations of calcium carbonate and calcium oxalate were made from solutions containing 5 g. of CaO per liter. The precipitates were washed by decantation with large volumes of redistilled water, time being given for diffusion of impurities from the solid, and the final wash water was separated by aid of the centrifuge. Calcium oxide was finally obtained from the carbonate or oxalate by ignition in platinum crucibles in an electric muffle. While determinations of the heat of solution in hydrochloric acid were made on eighteen different samples of calcium oxide, the data recorded in this

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[7] Richards and Thorvaldson, THIS JOURNAL, **37,** 81 (1915).

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

[9] Richards and Rowe, THIS JOURNAL, **42,** 1632 (1920).

[10] Richards and Thorvaldson, *ibid.,* **44,** 1057 (1922).

[11] Richards and Hönigschmid, *ibid.,* **32,** 1577 (1910).

paper in Table II represent the values obtained with four of the most carefully purified samples prepared from calcium salts from three widely different sources. Although the original materials contained only very small amounts of impurities, the process of purification in each case increased the heat of solution materially.

Sample A.—Calcium nitrate was recrystallized twice in vessels of fused silica. Calcium carbonate was then precipitated as calcite at room temperature with ammonium carbonate.

Sample B.—Calcium carbonate was dissolved in nitric acid. The neutral solution was treated with excess of bromine and milk of lime, boiled, filtered and the calcium nitrate recrystallized three times in vessels of fused silica. The calcium was precipitated as the carbonate by ammonium carbonate. The thoroughly washed and centrifuged calcium carbonate was dissolved in hydrochloric acid and precipitated as calcium oxalate.

Sample C.—A solution 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 nitrate was then recrystallized five times in glass, three times in platinum vessels and the calcium precipitated as calcium carbonate (calcite) by ammonium carbonate.

Sample D.—A portion of the calcium nitrate obtained after the eighth recrystallization of Sample C was precipitated by ammonium carbonate at the boiling point, crystals of aragonite being obtained.

Experimental Procedure

The experimental technique of adiabatic calorimetry is well known[6,8,9,10] and will not be described here. The method of introduction of the calcium oxide into the calorimeter should, however, be described. The calcium oxide, freshly ignited to constant weight, was dropped into the calorimeter vessel through a glass tube which reached through the cover of the calorimeter jacket. To the lower end of the glass tube there was attached a tube of gold foil which just made contact with the surface of the liquid in the calorimeter. It was found that any spattering of the liquid was caught by the gold tube. As soon as the calcium oxide had been introduced the gold tube was released and dropped into the acid solution, where it was held suspended from the cover to prevent it from interfering with the stirrer. The glass tube was then removed and the weight of any lime adhering to its inner surface, which generally did not exceed two or three milligrams, was determined by titration with standard

TABLE I

HEAT CAPACITY OF THE SYSTEM

	Specific heat	Heat capacity, cal./deg.
600.4 g. $HCl \cdot 200H_2O$	0.9821[a]	589.65
195.9 g. gold calorimeter and foil	.031[b]	6.07
14.5 g. stirrer (80% Au, 20% Cu)	.044[b]	0.64
0.3 g. air (1/2 of total)	.240[b]	.07
Thermometer		1.40
Total heat capacity		597.8

[a] Richards, Mair and Hall, THIS JOURNAL, **51**, 727 (1929).

[b] I. C. T., **1929**, Vol. V, pp. 81, 92, 120.

acid. The original weight of calcium oxide was then corrected for the amounts remaining in the crucible and adhering to the tube. The calcium oxide dissolved very rapidly, a constant stirring correction being usually reached in from six to eight minutes. A thermal head of 0.010 ± 0.005° was maintained between the jacket and the calorimeter vessel during the experiments.

All weights were corrected to vacuum. The calcium oxide was introduced at the final temperature of the reaction (20°) and is therefore not included in the heat capacity.

Table II

Heat of Solution of CaO in $HCl{\cdot}200H_2O$

Expt.	Sample of CaO	CaO, g.	Final temp., °C.	Temp. rise,[a] °C.	Heat of soln. 18° cal. per g. of CaO
1	A	2.9098	20.03	4.036	829.2
2	A	2.8976	20.00	4.019	829.2
3	A	2.9352	20.05	4.064	827.7
4	B	2.9410	20.13	4.072	827.7
5[b]	B	2.9155	19.95	3.976	828.9
6	B	2.8859	20.00	3.998	828.2
7	C	2.8870	19.97	3.998	827.8
8	C	2.8701	19.93	3.973	827.5
9	C	2.8609	19.95	3.965	828.5
10	C	2.8483	19.97	3.945	828.0
11	D	2.9703	19.98	4.121	829.4
12	D	2.9732	20.03	4.122	828.8
13	D	2.8974	20.06	4.024	830.2
14	D	2.7087	19.93	3.757	829.2
		Average	20.00	4.005	828.6

[a] 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.

[b] Heat capacity in Expt. 5 was 607.8 cal./deg.

Discussion of Experimental Results

The average value from Table II represents the isothermal heat of reaction at the final temperature 20.00°, expressed in terms of the mean calorie between 16 and 20°.

One further correction should be applied to this value. The volume of air enclosed in the calorimeter system was about 500 cc., one-half of which was included in the calculated heat capacity of the system. Assuming that this volume of air was completely saturated with water vapor both at the beginning and at the end of an experiment, the heat absorbed by evaporation would be 1.1 calories, which is equivalent to approximately 0.4 calorie per gram of calcium oxide. As thermal equilibrium is attained rather rapidly at the end of the run, it would probably be more nearly correct to apply three-fourths of the calculated correction.

Applying a correction of 0.3 calorie per gram, the final value for the isothermal heat of solution of calcium oxide in $HCl \cdot 200H_2O$ at 20° becomes 828.9 calories per gram (mean calorie 16 to 20°). This is equivalent to 194.4 kj. or 46.50 cal.$^{20°}$ per mole.

The samples of calcium oxide used in Expts. 9 and 10 were heated at 1200° for three hours after being brought to constant weight in the usual way at 800 to 900°. In another case a sample was heated at 1200° for twenty-four hours without giving an appreciable change in the heat of solution. The results indicate that the heat of solution is not materially affected by the temperature of ignition between the limits 800 and 1200°.

Summary

The heat of solution of calcium oxide in $HCl \cdot 200H_2O$ at 20° was found to be 194.4 kilojoules or 46.50 cal.$^{20°}$ per mole. The heat of solution was found not to be materially affected by the temperature of ignition between 800 and 1200°.

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THE IODOMETRIC DETERMINATION OF IRON

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Introduction

In the course of an investigation the demand arose for a rapid, fairly accurate method of determining iron in a precipitate of ferric hydroxide. A review of the various volumetric processes for determining iron was therefore made. Oxidation methods, using standard permanganate or dichromate solutions, involve the preliminary reduction of the ferric solution. In the reduction methods solutions of stannous chloride or of a titanous salt are commonly used, but both of these solutions are so unstable as to require frequent standardization or elaborate precautions in storage. The use of sodium thiosulfate for the direct titration of a ferric salt has been investigated,[1] but the conditions under which accurate results can be obtained are apparently very strictly limited.[2] An iodometric method, in which iodide is added to a ferric salt solution and the liberated iodine titrated with thiosulfate, was originally proposed by Mohr.[3]

The iodometric method appeared to offer great advantages, provided a simple process giving exact results could be found. However, experiments

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[1] Kremer, *J. prakt. Chem.*, **84**, 339 (1861).

[2] Norton, *Am. J. Sci.*, **18**, 25 (1899).

[3] Mohr, *Ann. Chem. Pharm.*, **105**, 53 (1858).