TABLE I

THE HYDROLYSIS OF ACETYLATED HYDROXY ACIDS

$\sqrt{\mu}$	$k_{obs.}$	k_0 (calcd. by (4))
Acetylmandelic		
0.107	1.26	1.01
.150	1.32	0.98
.150	1.31	.97
.221	1.48	.97
β-Acetoxy-β-phenyl-propionic		
0.108	1.23	0.98
.153	1.32	.97
.156	1.29	.95
.218	1.47	.98
α-Acetoxy-β-phenyl-propionic		
0.111	0.566	0.450
.158	.622	.454
.222	.662	.437
Acetylsalicylic		
0.110	7.26	5.78
.153	7.36	5.42
.157	7.29	5.34
.218	8.09	5.47
Acetylbenzilic		
0.123	0.01550	0.0120
.175	.01627	.0116
.176	.0166	.0118
.177	.01609	.0114
.247	.01744	.0110
Acetylglycolic		
0.166	3.32	2.39
.206	3.45	2.33
.235	3.58	2.31
1-Acetylmalic		
0.260	0.191	0.0738
.368	.242	.0703

obtained by La Mer and Greenspan are in quantitative agreement with the Brönsted theory. It seems probable that if the experiments could be carried out in sufficiently dilute solution agreement with equation (1) would be obtained.

Equation (3) may prove a convenience in extrapolation, for kinetic measurements of this sort. In the study of the addition of hydrobromic acid to glycid Brönsted, Kilpatrick and Kilpatrick[4] were able to obtain accurate results in sufficiently dilute solution to test and confirm equation (1). The data show a departure from (1) even below $\mu = 0.01$, but a plot corresponding to their Fig. 9, log k against $\sqrt{\mu}/(1 + \sqrt{\mu})$ rather than $\sqrt{\mu}$, shows agreement with equation (4) over the whole range studied. Calculation of log k_0 by equation (4) gives a constant value over the whole range, 0.592 ± 0.001.

Summary

It has been shown that one cannot conclude from the measurements of La Mer and Greenspan on the hydrolysis of the acetylated hydroxy acids that their results are not in quantitative agreement with the Brönsted theory.

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[4] Brönsted, Kilpatrick and Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

PHILADELPHIA, PA. RECEIVED AUGUST 6, 1934

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

Studies on the Thermochemistry of the Compounds Occurring in the System $CaO–Al_2O_3–SiO_2$. V. The Heats of Formation of Tricalcium Silicate and Dicalcium Silicate[1]

BY O. K. JOHANNSON AND T. THORVALDSON

Introduction

The only data found in the literature from which the heat of formation of tricalcium silicate can be calculated are those obtained by D. Tschernobaeff[2] by firing mixtures of calcium carbonate and silica (quartz) with charcoal in a bomb calorimeter. The average value obtained for the reaction between the calcium carbonate and the silica was 107.9 kg. cal. absorbed per mole of tricalcium silicate. Assuming that on dissociation of calcium carbonate 42.7 kg. cal. per mole are absorbed, the value obtained for the heat of formation of tricalcium silicate from calcium oxide and quartz is 20.2 kg. cal. per mole or 88.5 g. cal. per gram of tricalcium silicate. Tschernobaeff states that the reaction product contained both some combined carbon dioxide and "a great amount of free lime."

Tschernobaeff and Wologdine[3] used the same method to determine the heat of formation of dicalcium silicate. Their calculated value for the heat of formation from calcium oxide and silica (sand) was 28.7 kg. cal. per mole of Ca_2SiO_4.

Nacken[4] determined the heat of solution of γ-dicalcium silicate in a mixture of hydrochloric and hydrofluoric acids. The analysis of the artificially prepared silicate, the concentration of the solution of acids and the temperature of the determinations are not given. The average value recorded for the heat of solution was 537.304 calories per gram or 92.671 kg. cal. per mole of γ-dicalcium silicate. From this value and the heat of solution of an equivalent amount of lime and silica

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

[2] D. Tschernobaeff, *Revue de Metallurgie*, **2**, 729 (1905).

[3] Tschernobaeff and Wologdine, *Compt. rend.*, **154**, 206 (1912).

[4] Nacken, *Zement*, **19**, 818, 847(1930).

in the same mixture of acids, Nacken calculated the heat of formation of γ-dicalcium silicate from lime and silica as 209.396 cal. per gram or 36.109 kg. cal. per mole. This value differs widely from the 28.7 kg. cal. per mole obtained by Tschernobaeff and Wologdine.[3]

Apparatus and Experimental Procedure

The calorimeter, which was of the Richards adiabatic type with slight modifications, the Beckmann thermometers used, the method of introducing the sample into the calorimeter and the limits of adiabatic control have been described elsewhere.[5] One new modification was introduced during this work. The rotary gold stirrer used to agitate the liquid contained in the gold calorimeter was driven by means of a small synchronous motor.[6] With careful regulation of the thermal head of the calorimeter jacket, the temperature rise due to stirring and transference of heat during thirty-minute periods was found to check within ±0.001°, or ±0.00003° per minute. All the work was done in a room maintained at a constant temperature of 21°. All weights were compared with a U. S. Bureau of Standards absolute standard and corrected to vacuum.

The silicates studied were gamma-dicalcium silicate, beta-dicalcium silicate and tricalcium silicate. The general procedure used was to determine the heat of solution (or decomposition) of the silicate in acid of the concentration $HCl \cdot 20H_2O$. The heats of dilution of the acid and of the resulting solution (containing the liberated silica gel) when diluted to a concentration corresponding to $HCl \cdot 200H_2O$ were then determined by the method of Richards, Rowe and Burgess,[7] and the heat of solution (or decomposition) of the silicate in $HCl \cdot 200H_2O$ calculated according to the usual method.[7] From this result and the known heat of solution of calcium oxide in $HCl \cdot 200H_2O$[5a] the heat of formation of the respective silicate from calcium oxide and silica gel was then calculated. The latent heat of transition of the beta to the gamma form of dicalcium silicate was also calculated.

About 95 to 99% of the total rise of temperature occurs, under the conditions of the experiments, during the first thirty minutes after the introduction of the finely powdered silicate into the acid in the calorimeter. Then follows a considerable interval, the length of which varies somewhat with different samples of the silicate, during which the rate of rise is considerably in excess of the initial rating for the heat of stirring. During this period, the rate of rise decreases slowly until it is equivalent to the initial rating. The possibility that this slow rise might be due to changes in the heat of stirring during the determination was excluded by experiments showing (1) that the viscosity of the calorimeter liquid did not vary appreciably and (2) that the presence of the silica in suspension did not affect the heat of stirring. The decomposition of the silicate was shown to be complete by the absence of non-volatile impurities in the precipitated silica (on treatment with hydrofluoric acid). Experiments with a solution of sodium silicate, in place of the solid silicate of calcium, demonstrated that at least a considerable portion of the slow rise after the first thirty minutes of a determination must be due to the thermal changes in the silica after the decomposition is completed. While the time required from the introduction of the sample until the rate of rise in temperature reached the initial stirring correction varied from one and one-half to three hours, the experiments were always continued for an hour to an hour and a half longer. With the synchronous motor and such long initial and final rating periods, the possibility of slow thermal changes equivalent to more than 0.00002° per minute was excluded definitely.

Preparation of the Silicates.—Finely ground mixtures of calcium carbonate and silica in the proper proportions were moulded into hollow cylinders. These were dried and then fired, supported on a disk of magnesium oxide, in a compressed air-oil furnace at temperatures between 1500–1600° until well sintered. The cylinder was then either allowed to dust (in the case of dicalcium silicate) or crushed in a tool steel mortar, any steel removed by a magnet, and the product ground in an agate mortar to pass a 200-mesh sieve. The cylinder was then remade and refired until a satisfactory product free from uncombined lime was obtained.[8,9] In preparing the tricalcium silicate the lime content was increased gradually according to the method described by Lerch and Bogue.[10]

The usual method of preventing the transition of β-Ca_2SiO_4 to γ-Ca_2SiO_2 is to add either boric acid or chromic oxide and to quench the product. Such additions are undesirable in the case of thermochemical material. An intimate mixture of pure calcium carbonate and very light silica gel gave after one firing a product which did not invert to the γ-form on rapid quenching. This sample (β-$CaSiO_2$ "A") was very pure, contained no free lime and only traces of the γ-form and free silica.

It was also found that the β-form could be prepared entirely free from any of the γ-variety by heating a sample of the latter, ground to pass a 200-mesh sieve, at about 1000° for several hours and then cooling rapidly to room temperature. This is probably due to the decrease in the rate of conversion on account of the less intimate contact of the crystals in this fluffy material. Sample β-Ca_2SiO_4 "B" was prepared in this way from γ-Ca_2SiO_4 Sample "A." These two samples have therefore identical chemical composition and the results obtained with them give directly the heat of transition of the β to the γ-form.

The authors are indebted to Dr. V. A. Vigfusson for careful microscopic examination of the substances prepared. The refractive indices were carefully checked in each case.

The analyses of the various samples are given in Table I as well as a calculation of the compounds present as impurities in each sample by a method similar to that of

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(5) (a) Thorvaldson, Brown and Peaker, THIS JOURNAL, **51**, 2678 (1929); (b) Thorvaldson and Brown, *ibid.*, **52**, 80 (1930); (c) Thorvaldson, Brown and Peaker, *ibid.*, **52**, 3927 (1930).

(6) E. L. Harrington, American Physics Teacher, Dec., 1934. The authors wish to express their indebtedness to Professor Harrington for supplying this motor.

(7) Richards Rowe and Burgess, THIS JOURNAL, **32**, 1176 (1910).

(8) A. H. White, *J. Ind. Eng. Chem.*, **1**, 5 (1909).

(9) Lerch and Bogue, *ibid.*, **18**, 739 (1926); *ibid.*, *Anal. Ed.*, **2**, 296 (1930).

(10) Lerch and Bogue, *J. Phys. Chem.*, **31**, 1627 (1927).

Bogue.[11] Certain evident assumptions as to the compounds present in each case are made.

TABLE I

ANALYSES OF THE SILICATES[a] (ANHYDROUS BASIS)

	β-Dicalcium silicate "A"	γ-Dicalcium silicate "A" β-dicalcium silicate "B"	Tricalcium silicate	
			"A"	"B"
SiO_2[b]	34.45	34.99	26.71	26.64
CaO[c]	64.17	62.62	72.52	71.97
Al_2O_3	0.75	1.14	0.76	0.80
Fe_2O_3	Trace	Trace	Trace	Trace
MgO	0.50	1.29	0.26	0.57
Free SiO_2	.19	....	Trace	.05
	100.06	100.04	100.25	100.03
MgO	0.50	1.29	0.26	0.57
SiO_2	.19	....	Trace	.05
$CaO \cdot Al_2O_3$	1.16	1.76	....	....
$3CaO \cdot Al_2O_3$	....	....	2.01	2.12
$CaO \cdot SiO_2$	1.20	6.92	....	....
$2CaO \cdot SiO_2$	97.01	90.07	10.90	12.21
$3CaO \cdot SiO_2$	....	....	87.08	85.08
	100.06	100.04	100.25	100.03

[a] The analytical procedure was that recommended by Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, 1929.

[b] Total silica less silica in "insoluble residue," determined according to U. S. Gov. specification for Portland cement.

[c] None of the samples contained any free calcium oxide.[8,9]

The Determination of the Heats of Decomposition of the Silicates in $HCl \cdot 20H_2O$ and in $HCl \cdot 200H_2O$.—Tables II and III give a summary of the experimental results and the calculations of the heats of decomposition of the pure silicates. For a detailed example of the method of calculating the heat of decomposition of a silicate in $HCl \cdot 200H_2O$ from its heat of decomposition in $HCl \cdot 20H_2O$ and the heats of dilution of the initial and the final systems, the reader is referred to a similar case, an aluminate of calcium, in a previous paper of this series.[5c]

For the purpose of calculating the heat of decomposition of a pure sample of the silicate in $HCl \cdot 200H_2O$, it is assumed that the heats of decomposition or solution of the components of a mixture in acid of this dilution are additive. It has been shown repeatedly that the mixing of hydrochloric acid solutions of this concentration with similar solutions in which a portion of the acid hydrogen has been replaced by a metal does not give an appreciable thermal effect. However, should there be any tendency for the formation of solid solutions such admixtures may affect the value of the lattice energy of the solid. The agreement of the calculated results for the heat of decomposition of pure β-dicalcium silicate from the experimental results for samples "A" and "B" and the similar agreement in the case of the two products containing mainly tricalcium silicate indicate that such an effect is not marked for these silicates.

Approximate values for the heat of solution or decomposition of tricalcium aluminate, monocalcium aluminate, monocalcium silicate and magnesium oxide in $HCl \cdot 200H_2O$ were necessary for these calculations. The first has already been determined[5c] (733 cal. per g.). Approximate values for the second and third were determined (636 and 191 cal. per g., respectively) and a value for magnesium oxide (812 cal. per g.) was calculated from available data.[12]

Calculation of Heats of Formation and Transition.—Taking the average value for the heat of decomposition of β-dicalcium silicate Samples "A" and "B," namely, 347 g. cal. per gram or 59.76 kg. cal. per mole, and the value 56.50 kg. cal. per mole for the heat of solution of calcium oxide in $HCl \cdot 200H_2O$,[5a] one obtains the figure 33.24 kg. cal. (139.0 kj.) per mole or 193.0 g. cal. (807 j.) per gram for the heat of formation at 20° of β-Ca_2SiO_4 from calcium oxide and silica gel.

From the value 341.0 g. cal. per gram or 58.73 kg. cal. per mole, for the corresponding heat of decomposition of γ-dicalcium silicate in $HCl \cdot 200H_2O$, one obtains the figure 34.27 kg. cal. (143.3 kj.) per mole or 199.0 g. cal. (832 j.) per gram for the heat of formation at 20° of γ-Ca_2SiO_4 from calcium oxide and silica gel.

From the above one obtains the value 1.03 kg. cal. (4.3 kj.) per mole or 6 g. cal. (25 j.) per gram for the heat of transition at 20° of the β- to the γ-form of dicalcium silicate. This is in qualitative agreement with the fact that γ-dicalcium silicate is the stable form at ordinary temperatures. The value obtained directly from the data for β-dicalcium silicate "B" and γ-dicalcium silicate "A," *i. e.*, 5.5 g. cal. (23 j.) per gram, may be more reliable since these samples are of identical chemical composition.

From the value 467.5 g. cal. per gram or 106.73 kg. cal. per mole for the heat of decomposition of tricalcium silicate in $HCl \cdot 200H_2O$ one obtains the figure 32.77 kg. cal. (137.0 kj.) per mole or 143.5 g. cal. (600 j.) per gram for the heat of

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(11) Bogue, *Ind. Eng. Chem., Anal. Ed.*, **1**, 192 (1929).

(12) "I. C. T.," 1929, Vol. V, pp. 176 and 195.

TABLE II

HEATS OF DECOMPOSITION OF DICALCIUM SILICATE AND TRICALCIUM SILICATE IN $HCl\cdot 20H_2O$

Description of sample	Detns.	Av. wt. of anhydrous silicate per 600.6 g. acid	Av. final temp., °C.	Av. corr. rise, °C.	Av. heat capacity, 19° cal.	Av. heat of decompn. at 20°, 19° cal./g.	Variation of extremes from av., cal./g.
β-$2CaO\cdot SiO_2$ "A"	4	3.0065[a]	20.2	2.0605	519.3	356.0	+0.5 −0.3
β-$2CaO\cdot SiO_2$ "B"	4	2.8955[a]	20.1	1.9645	519.3	352.3	+0.9 −0.8
γ-$2CaO\cdot SiO_2$ "A"	10	2.9480[b]	20.0	1.9702	519.6	347.2	+1.7 −1.2
$3CaO\cdot SiO_2$ "A"	5	2.2195[c]	20.1	2.0054	519.3	469.2	+1.9 −1.5
$3CaO\cdot SiO_2$ "B"	4	2.2137[c]	20.2	1.9940	519.3	467.8	+0.8 −0.8

[a] Ignited samples. [b] Samples corrected for loss on ignition. [c] Samples were ignited for thirty minutes at 800 to 900°. Tests for free lime were negative except in two cases where traces were present after ignition. See Carlson, *Bur. Standards J. of Res.*, **7**, 893 (1931).

TABLE III

HEATS OF DECOMPOSITION OF DICALCIUM SILICATE AND TRICALCIUM SILICATE IN $HCl\cdot 200H_2O$

Description of sample	Av. heat of decompn. in $HCl\cdot 20H_2O$ cal./g.	Av. wt. of $HCl\cdot 20H_2O$ per gram silicate	Av. rise of temp. in dilution experiment final soln., °C.	Av. heat of diln. of initial $HCl\cdot 20H_2O$[a] to $HCl\cdot 200H_2O$, cal./g. of silicate	Av. heat of diln. of final soln.,[b] cal./g. of silicate	Calcd. heat of decompn. of silicate sample in $HCl\cdot 200H_2O$, cal./g.	Calcd. heat of decompn. of pure silicate in $HCl\cdot 200H_2O$, cal./g.
β-$2CaO\cdot SiO_2$ "A"	356.0	199.8	0.1483	278.1	273.0	350.9	347.5
β $2CaO\cdot SiO_2$ "B"	352.3	207.4	.1483	288.7	283.4	347.0	346.5
γ-$2CaO\cdot SiO_2$ "A"	347.2	204.0	.1483	283.9	278.7	342.0	341.0
$3CaO\cdot SiO_2$ "A"	469.2	270.6	.1481	376.6	369.1	461.7	467.5
$3CaO\cdot SiO_2$ "B"	467.8	271.3	.1481	377.6	370.0	460.2	467.5

[a] 61.22 g. $HCl\cdot 20H_2O$ diluted to $HCl\cdot 200H_2O$ (total heat cap. 564.2 cal./g.) gave average rise of 0.1510°.

[b] 61.44 g. of final solution used. Total heat capacity 564.3 cal./g.

formation at 20° of tricalcium silicate from calcium oxide and silica gel.

While the formation of these silicates from calcium oxide and silica gel involves the evolution of heat, one finds from the data for the heats of solution that the formation of tricalcium silicate from calcium oxide and β-dicalcium silicate involves the absorption of 0.47 kg. cal. (2.0 kj.) per mole or 2.06 g. cal. (8.6 j.) per gram, the corresponding figures with γ-dicalcium silicate being an absorption of 1.50 kg. cal. (6.3 kj.) per mole or 6.59 g. cal. (27.5 j.) per gram of tricalcium silicate. It has been shown[13] that tricalcium silicate is unstable and decomposes into lime and dicalcium silicate at temperatures between 1000 and 1300°. The thermochemical results indicate that tricalcium silicate is metastable with respect to calcium oxide and dicalcium silicate at 20°.

Summary

1. A new method for the preparation of the β-form of dicalcium silicate is described.

2. The isothermal heats of decomposition of samples of β- and γ-dicalcium silicate and tricalcium silicate in $HCl\cdot 20H_2O$ were determined and the heats of decomposition of the same substances in the pure state in $HCl\cdot 200H_2O$ were calculated.

3. The following thermochemical quantities were calculated: (a) the isothermal heats of formation at 20° of β-dicalcium silicate, γ-dicalcium silicate and tricalcium silicate from calcium oxide and silica gel; (b) the isothermal heats of formation at 20° of tricalcium silicate from calcium oxide and the two above forms of dicalcium silicate; (c) the heat of transition at 20° of β-dicalcium silicate to γ-dicalcium silicate.

4. The results indicated that at 20° β-dicalcium silicate is metastable with respect to γ-dicalcium silicate and tricalcium silicate is metastable with respect to calcium oxide and both the forms of dicalcium silicate.

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(13) Carlson, *Bur. of Standards J. Research*, **7**, 893 (1931).