

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Crystalline Calcium Orthosilicate, Tricalcium Silicate and Zinc Orthosilicate¹

BY E. G. KING

In an earlier paper, Torgeson and Sahama² reported heat-of-formation values for crystalline calcium metasilicate and magnesium ortho- and metasilicates. In continuance of this work, the present paper contains results for crystalline calcium orthosilicate, tricalcium silicate and zinc orthosilicate. The calcium compounds were studied previously by Johannson and Thorvaldson,³ who obtained heats of formation from calcium oxide and silica gel, rather than the more desirable calcium oxide and quartz. Earlier data for zinc orthosilicate⁴ indicate a heat of formation from the oxides of opposite sign from that expected from other known properties of this substance.

Materials and Method

Calcium orthosilicate (β -variety)⁵ was prepared from reagent-grade calcium carbonate and natural quartz (99.9% pure). The finely ground and intimately mixed substances were heated in alundum for some 20 days at 1350°, with intermittent grinding, mixing and analyses for adjustment of composition. The final product gave an X-ray diffraction pattern agreeing in all respects with that of Clark⁴ for the β -variety. There was no evidence of the low density, gamma-modification, and the "dusting" phenomenon usually encountered was completely absent. This is attributed, in part, to the prolonged heating at 1350° which afforded opportunity for good crystal growth. Analysis showed 64.47% CaO, 34.68% SiO₂, 0.32% R₂O₃, 0.14% MgO and 0.02% ignition loss. (Theoretical anal. 65.13% CaO; 34.87% SiO₂).

Tricalcium silicate was prepared from reagent-grade calcium carbonate and natural quartz, following the directions of Hansen.⁷ The ingredients were heated in platinum for a total of 10 hours at 1500°, with intermittent grinding, mixing and adjustment of composition. The analysis of the product was 73.64% CaO, 26.21% SiO₂, 0.13% R₂O₃, 0.11% MgO and 0.05% ignition loss (theoretical anal. 73.69% CaO; 26.31% SiO₂). A free lime content of 0.3% was found by the method of Lerch and Bogue.⁸ The X-ray diffraction pattern agreed with the work of Hansen.⁷

The zinc orthosilicate (willemite) was a synthetic product furnished by the Geophysical Laboratory of the Carnegie Institution of Washington. A small adjustment of composition was made, and the material was given two 15-hour heats at 1000° with intermittent mixing. The final analysis showed 72.88% ZnO and 26.94% SiO₂, as compared with the theoretical 73.05 and 26.95%, respectively. The X-ray diffraction pattern was compared with that of natural willemite and with values in the A.S.T.M. index. No lines other than those of willemite were observed.

Calcium oxide was prepared from reagent-grade calcium carbonate by ignition for 12 hours at 1100°. The ignition was made just before each measurement, so that it was necessary to store the product for only 1 or 2 hours. This was done in a desiccator over phosphorus pentoxide.

Reagent-grade zinc oxide was employed. It was heated at 1100° for 3 hours in a stream of nitrogen.

The quartz was the purest available grade of natural mineral. It was ground to -325 mesh, and water-elutriated for 3 hours to eliminate the coarser particles, and finally dried at 180°. Upon a completely dry basis, the product was 99.9% SiO₂. As used, 0.4% water was present for which correction was made in the measurements.

The heats of formation were determined by measuring the heats of reaction of the silicates and their constituent oxides with 20.1% hydrofluoric acid, at 73.7° in the case of the calcium compounds and at 50.0° for the zinc compound. In all instances, 940.1 g. of the acid was employed. The masses of the other materials conformed stoichiometrically with 0.7420 g. of quartz, which was used as a basis. The samples were contained in gelatin capsules for dropping into the calorimeter. Corrections for the capsules were made from separate measurements of the heat of solution of gelatin.

The apparatus was essentially that described by Torgeson and Sahama.² The only alterations were (1) a new solution vessel about 10% larger in volume, constructed of platinum-10% rhodium alloy, (2) a new outer housing of heavier design, constructed of Monel metal, and (3) an improved system of thermostat control using a Micro-set differential thermo-regulator and a microampere galvanometer relay. The thermostat temperature varied only $\pm 0.02^\circ$ during the present measurements and this resulted in considerable improvement in operation of the calorimeter and in heat interchange corrections.

Measurements and Results

All values are in terms of the defined calorie (1 cal. = 4.1833 int. joules). All weighings were reduced to vacuum and all molecular weights accord with the 1949 International Atomic Weights.

Each heat of formation is the resultant of the measurements of a series of reactions for which skeleton equations are given in Tables I, II and III. The precision uncertainties have been calculated according to the methods of Rossini and Deming.⁹

Calcium Orthosilicate.—Table I presents the data for obtaining the heat of formation of calcium orthosilicate.

TABLE I
HEAT OF FORMATION OF Ca₂SiO₄(β)(CAL./MOLE)

Reaction	ΔH	Uncertainty
(1) 2CaO (<i>c</i> , 25°) + 4HF (sol., 73.7°) → 2CaF ₂ (ppt., 73.7°) + 2H ₂ O (sol., 73.7°)	-110,740	70
(2) Ca ₂ SiO ₄ (β , 25°) + 10HF (sol., 73.7°) → 2CaF ₂ (ppt., 73.7°) + H ₂ SiF ₆ (sol., 73.7°) + 4H ₂ O (sol., 73.7°)	-113,840	200
(3) SiO ₂ (<i>c</i> , 35°) + 6HF (sol., 73.7°) → H ₂ SiF ₆ (sol., 73.7°) + 2H ₂ O (sol., 73.7°)	- 33,290	80
(4) 2CaO (<i>c</i> , 25°) + SiO ₂ (<i>c</i> , 25°) → Ca ₂ SiO ₄ (β , 25°)	- 30,190	230

$$\Delta H_4 = \Delta H_1 - \Delta H_2 + \Delta H_3$$

Six determinations of the heat of reaction (1) were made. The results are -110,680, -110,740,

(9) Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(1) Not copyrighted.

(2) Torgeson and Sahama, *THIS JOURNAL*, **70**, 2156 (1948).

(3) Johannson and Thorvaldson, *ibid.*, **56**, 2327 (1934).

(4) National Bureau of Standards Tables of Selected Values of Chemical Thermodynamic Properties, Series I, Table 31-13 (Dec. 31, 1948).

(5) Preparation and analysis of this material was conducted by K. R. Bonnickson, Pacific Experiment Station.

(6) Clark, *J. Am. Ceram. Soc.*, **29**, 25 (1946).

(7) Hansen, *ibid.*, **11**, 68 (1928).

(8) Lerch and Bogue, *Ind. Eng. Chem., Anal. Ed.*, **2**, 296 (1930).

-110,700, -110,660, -110,860 and -110,820, the mean being -110,740 \pm 70 cal.

Six measurements were made of reaction (2), the results being -113,860, -113,710, -113,540, -113,870, -114,270 and -113,810. The mean is -113,840 \pm 200 cal.

Seven determinations of reaction (3) gave -33,200, -33,390, -33,100, -33,320, -33,280, -33,390 and -33,330 cal. The mean is -33,290 \pm 80. These values include a -33 cal. correction for the water content of the quartz.

The heat of formation of β -calcium orthosilicate from calcium oxide and quartz is given by $\Delta H_1 - \Delta H_2 + \Delta H_3$ and is -30,190 \pm 230 cal./mole. It should be noted that, from the nature of the skeleton reactions, this value is for 25° (298.16°K.).

Tricalcium Silicate.—Skeleton equations of the reactions and the data for obtaining the heat of formation of tricalcium silicate appear in Table II.

TABLE II
HEAT OF FORMATION OF Ca_3SiO_5 (CAL./MOLE)

Reaction	ΔH	Uncertainty
(5) $3\text{CaO} (c, 25^\circ) + 6\text{HF} (\text{sol.}, 73.7^\circ) \rightarrow 3\text{CaF}_2 (\text{ppt.}, 73.7^\circ) + 3\text{H}_2\text{O} (\text{sol.}, 73.7^\circ)$	-165,370	140
(6) $\text{Ca}_3\text{SiO}_5 (c, 25^\circ) + 12\text{HF} (\text{sol.}, 73.7^\circ) \rightarrow 3\text{CaF}_2 (\text{ppt.}, 73.7^\circ) + \text{H}_2\text{SiF}_6 (\text{sol.}, 73.7^\circ) + 5\text{H}_2\text{O} (\text{sol.}, 73.7^\circ)$	-171,680	150
(7) $\text{SiO}_2 (c, 25^\circ) + 6\text{HF} (\text{sol.}, 73.7^\circ) \rightarrow \text{H}_2\text{SiF}_6 (\text{sol.}, 73.7^\circ) + 2\text{H}_2\text{O} (\text{sol.}, 73.7^\circ)$	-33,290	80
(8) $3\text{CaO} (c, 25^\circ) + \text{SiO}_2 (c, 25^\circ) \rightarrow \text{Ca}_3\text{SiO}_5 (c, 25^\circ)$ $\Delta H_8 = \Delta H_5 - \Delta H_6 + \Delta H_7$	-26,980	220

Five determinations were made for reaction (5): -165,180, -165,330, -165,270, -165,540 and -165,510 cal. The mean is -165,370 \pm 140.

For reaction (6), the following seven determinations were made: -171,820, -171,460, -171,620, -171,650, -171,430, -171,880 and -171,870. The mean is -171,680 \pm 150 cal.

Reaction (7) is the same as reaction (3). It should be noted that ΔH_7 differs from $3/2\Delta H_1$ because of the difference in concentration of the final solution.

The heat of formation of tricalcium silicate from calcium oxide and quartz at 25° (298.16°K.) is $\Delta H_5 - \Delta H_6 + \Delta H_7 = -26,980 \pm 220$.

Zinc Orthosilicate.—Table III lists the skeleton equations and data for obtaining the heat of formation of zinc orthosilicate.

Seven measurements of the heat of reaction (9) were made. The results are -44,780, -44,800, -44,900, -45,080, -44,800, -44,880 and -44,920, the mean being -44,880 \pm 80 cal.

Six measurements of the heat of reaction (10) gave -70,650, -70,780, -70,720, -70,630, -70,660 and -70,770 cal. The mean is -70,700 \pm 60.

For reaction (11), six measurements resulted in -32,840, -32,750, -32,670, -32,890, -32,960 and -32,730 cal., the mean value being -30,810 \pm 90. These values contain a correction of -27

TABLE III
HEAT OF FORMATION OF Zn_2SiO_4 (CAL./MOLE)

Reaction	ΔH	Uncertainty
(9) $2\text{ZnO} (c, 25^\circ) + 4\text{HF} (\text{sol.}, 50^\circ) \rightarrow 2\text{ZnF}_2 (\text{sol.}, 50^\circ) + 2\text{H}_2\text{O} (\text{sol.}, 50^\circ)$	-44,880	80
(10) $\text{Zn}_2\text{SiO}_4 (c, 25^\circ) + 10\text{HF} (\text{sol.}, 50^\circ) \rightarrow 2\text{ZnF}_2 (\text{sol.}, 50^\circ) + \text{H}_2\text{SiF}_6 (\text{sol.}, 50^\circ) + 4\text{H}_2\text{O} (\text{sol.}, 50^\circ)$	-70,700	60
(11) $\text{SiO}_2 (c, 25^\circ) + 6\text{HF} (\text{sol.}, 50^\circ) \rightarrow \text{H}_2\text{SiF}_6 (\text{sol.}, 50^\circ) + 2\text{H}_2\text{O} (\text{sol.}, 50^\circ)$	-32,810	90
(12) $2\text{ZnO} (c, 25^\circ) + \text{SiO}_2 (c, 25^\circ) \rightarrow \text{Zn}_2\text{SiO}_4 (c, 25^\circ)$ $\Delta H_{12} = \Delta H_9 - \Delta H_{10} + \Delta H_{11}$	-6,990	140

cal. to account for the presence of water in the quartz. The difference between ΔH_{11} and ΔH_3 is attributable to the difference in solution temperatures.

The heat of formation of zinc orthosilicate (willemite) from zinc oxide and quartz at 25° (298.16°K.) is $\Delta H_9 - \Delta H_{10} + \Delta H_{11} = -6,900 \pm 140$ cal./mole.

Related Thermal Data

The values for the heats of formation of the silicates from the oxides may be converted to heats of formation from the elements by means of available data for the oxides. Values for the heats of formation of calcium oxide, quartz and zinc oxide, taken from the National Bureau of Standards Tables,¹⁰ are, respectively, -151,900, -205,400 and -83,170 cal./mole. These values lead to the results in the last column of Table IV.

TABLE IV HEATS OF FORMATION AT 298.16°K., CAL./MOLE		
Substance	From oxides	From elements
$\text{Ca}_3\text{SiO}_5 (\beta)$	-30,190 \pm 230	-539,400
Ca_3SiO_5	-26,980 \pm 220	-688,100
Zn_2SiO_4	-6,990 \pm 140	-378,700

The National Bureau of Standards Tables¹¹ list -538,000 and -688,400 cal./mole, respectively, for the two calcium silicates. These figures presumably are based upon the work of Johannson and Thorvaldsen.⁴ There also is listed⁵ -360,800 cal./mole as the heat of formation of crystalline zinc orthosilicate from the elements. This value corresponds to a heat of formation from the oxides of $\Delta H_{298.16} = 10,940$, indicating that zinc orthosilicate is unstable with respect to the constituent oxides. This is contrary to general knowledge concerning willemite which indicates that it is stable from room temperature to the melting point, 1785°K.¹² The present value confirms the stability at room temperature.

It is of interest to compare successive steps of

(10) National Bureau of Standards Tables of Selected Values of Chemical Thermodynamic Properties, Series I, Tables 87-1 (Mar. 31, 1950), 24-2 (Sept. 30, 1948) and 31-1 (Dec. 31, 1948).

(11) *Ibid.*, Table 87-12 (Mar. 31, 1950).

(12) Silverman, Morey and Rossini, National Research Council Bulletin 107, June 1943.

addition of calcium oxide to form the series CaSiO_3 , Ca_2SiO_4 and Ca_3SiO_5 . Torgeson and Sahama² obtained $\Delta H_{298.16} = -21,250$ for the first step, $\text{CaO} + \text{SiO}_2$ (quartz) = CaSiO_3 (wollastonite). For $\text{CaO} + \text{CaSiO}_3$ (wollastonite) = $\text{Ca}_2\text{SiO}_4(\beta)$, $\Delta H_{298.16} = -8,940$; and for $\text{CaO} + \text{Ca}_2\text{SiO}_4(\beta) = \text{Ca}_3\text{SiO}_5$, $\Delta H_{298.16} = 3,210$. The heat of the last step is positive and, as the entropy change would be expected to be quite small, tricalcium silicate evidently is unstable with respect to orthosilicate and calcium oxide at 298.16°K.

Summary

Measurements were made of the heats of reaction of calcium orthosilicate, tricalcium silicate, zinc orthosilicate, calcium oxide, zinc oxide and quartz with hydrofluoric acid.

The heats of formation of the silicates from the oxides were obtained as follows: $\text{Ca}_2\text{SiO}_4(\beta)$, $\Delta H_{298.16} = -30,190 \pm 230$; Ca_3SiO_5 , $\Delta H_{298.16} = -26,980 \pm 220$; and Zn_2SiO_4 (willemite), $\Delta H_{298.16} = -6,990 \pm 140$ cal./mole.

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The Salts of Perrhenic Acid. IV. The Group II Cations, Copper(II) and Lead(II)¹

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All of these salts except the perrhenates of beryllium and mercury(II) have been previously reported.^{2,3} However, the only property reported was composition, and no definite conclusions concerning degree of hydration were drawn.

Preparation of the Salts.—In most cases the hydroxide, oxide or carbonate of the metal was treated with a solution of perrhenic acid⁴ and the hydrated salt was crystallized by evaporating the solution at room temperature over calcium chloride. Beryllium perrhenate was prepared by treating the metal with perrhenic acid and hydrogen peroxide and warming the mixture. The first attempt resulted in a solution which contained a considerable excess of beryllium. Presumably, a soluble, basic beryllium perrhenate was obtained. An excess of perrhenic acid was used in a subsequent preparation of this salt. Mercury(II) perrhenate was prepared from mercury(II) oxide and perrhenic acid. An insoluble basic salt was produced. The normal salt was obtained by recrystallization from water containing an excess of perrhenic acid.

Hydrates.—The hydrates which separated from water solution at room temperature are listed in Table I. Strontium perrhenate monohydrate was the only lower hydrate isolated.

In most cases the water of hydration was determined from weight lost on dehydration. Most of the hydrates were stable enough so that well formed crystals could be air dried at ordinary indoor temperatures and humidities during winter. The hydrates of the perrhenates of zinc, cadmium, and copper(II) were deliquescent under these conditions, and the dehydration data were inconclusive. A satisfactory characterization was effected by noting the weight gained as the salts became hydrated over 60% sulfuric acid. The study of beryllium perrhenate dihydrate was discontinued, due to the health hazard involved,⁵ before a satisfactory characterization was made. The agreement of the

water found with the calculated value shown in Table I is possibly fortuitous since this value is the average of two divergent determinations, 6.09 and 7.16%. Strontium perrhenate monohydrate was formed when the dihydrate was exposed to the ambient air. The monohydrate was stable over calcium chloride and was dehydrated by heating in an oven at 105°. The dehydration curves gave no indication of lower hydrates for the other salts. Barium perrhenate tetrahydrate and lead(II) perrhenate dihydrate were completely dehydrated when exposed to the ambient air. All of the other hydrates, with the exception of strontium perrhenate dihydrate, were completely dehydrated over calcium chloride. Completeness of dehydration was verified by either igniting the anhydrous residues at 600° or by analyzing them for perrhenate and the cation.

Analysis of the Salts.—All analyses were run in duplicate and good precision was obtained. Standard analytical methods were satisfactory for a majority of the salts, but in some cases it was necessary to develop special procedures. For the determination of perrhenate, a modification of the method of Willard and Smith⁶ was directly applicable to all but the perrhenates of zinc, cadmium, mercury(II) and lead(II). Lead was removed as the sulfate to prevent the precipitation of lead(II) chloride when tetraphenylarsonium chloride was added. Zinc and cadmium were removed and determined as 8-hydroxyquinolates. Their removal was necessary since they form precipitates with tetraphenylarsonium chloride.⁷ Tests on standard samples revealed that the excess 8-hydroxyquinoline in the filtrate from the cation determinations did not interfere with the perrhenate determination.

Attempts to remove mercury quantitatively as the 8-hydroxyquinolate were unsuccessful. Simultaneous precipitation of mercury(II) with tetraphenylarsonium chloride, suggested by a similar procedure developed for thallium(I) perrhenate,⁸ was unsatisfactory since no wash liquid was found which did not dissolve the mercury precipitate. In

(1) This paper is based on a dissertation presented by Grover E. Maxwell to the Graduate School of the University of Tennessee in partial fulfillment of the requirements for the Ph.D. degree, June, 1950.

(2) Wilke-Dorfurt and Gunzert, *Z. anorg. allgem. Chem.*, **216**, 369 (1933).

(3) Briscoe, Robinson and Rudge, *J. Chem. Soc.*, 2211 (1931).

(4) Smith and Maxwell, *This Journal*, **71**, 578 (1949).

(5) Stokinger, *Nucleonics*, **5**, No. 6, 53 (1949).

(6) Willard and Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 305 (1939).

(7) Willard and Smith, *ibid.*, **11**, 269 (1939).

(8) Smith, *Anal. Chem.*, **20**, 937 (1948).