

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Crystalline Silicates of Strontium and Barium

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Heats of formation from the component oxides at 298.15°K. were obtained for strontium metasilicate, strontium orthosilicate, barium metasilicate, barium orthosilicate, dibarium trisilicate and barium disilicate by measuring heats of reaction of the silicates and oxides with hydrofluoric acid.

This paper presents heats of formation of two crystalline strontium silicates (SrSiO_3 and Sr_2SiO_4) and four crystalline barium silicates (BaSiO_3 , Ba_2SiO_4 , $\text{Ba}_2\text{Si}_3\text{O}_8$ and BaSi_2O_5). Previous papers from this Laboratory by Torgeson and Sahama¹ and King² contained corresponding data for some magnesium and calcium silicates.

Materials and Method

The silicates were prepared by repeated, prolonged sintering of stoichiometric mixtures of reagent-grade strontium or barium carbonate and pure quartz. In each instance several heats were required, with intervening grinding, mixing, analysis and adjustment of composition, to obtain a satisfactory product.

In preparing strontium metasilicate the total heating time was 246 hr. between 1000 and 1350°, of which 32 hr. were above 1200°. The product gave an X-ray diffraction pattern agreeing virtually perfectly with that reported by Carlson and Wells.³ Chemical analysis gave 63.26% strontium oxide, 36.66% silica and 0.12% iron and aluminum oxides (theoretical analysis, 63.30% strontium oxide and 36.70% silica).

Strontium orthosilicate required four heats totaling 35 hr. at 1200–1300°, which were conducted in a platinum vessel. X-Ray diffraction of the product gave no evidence of uncombined oxides, but the pattern disagreed with that of O'Daniel and Tscheischwili,⁴ who may have had a different crystalline variety. Analysis gave 77.51% strontium oxide, 22.47% silica and 0.03% sodium oxide (theoretical analysis, 77.52% strontium oxide and 22.48% silica).

The stoichiometric mixture for the preparation of barium metasilicate was pelletized and heated nine times for a total of 247 hours between 1000 and 1410°, of which 48 hours were above 1200°. Silverman and co-workers⁵ list two crystalline varieties of barium metasilicate. Austin⁶ obtained the X-ray diffraction pattern of one variety, but that of the other has not been reported in the literature. The pattern for the present material showed no evidence of uncombined oxides but disagreed with that of Austin, indicating that it probably is the variety labeled " $\text{BaO}\cdot\text{SiO}_2(\text{II})$ " by Silverman and co-workers. Analysis gave 71.95% barium oxide and 28.17% silica, as compared with the theoretical 71.85 and 28.15%.

Barium orthosilicate was prepared in a nickel crucible; the stoichiometric mixture was heated five times for a total of 10 days at 1000–1150° and 16 hours at 1150–1300°. There was some attack of the crucible, making it necessary to discard the surface layer after each heat. The cleaned product gave no visible precipitate of nickel glyoxime from a 1-g. sample. The X-ray diffraction pattern agreed with that reported by Austin.⁶ Analysis showed 83.78% barium oxide and 16.39% silica, as compared with the theoretical 83.62 and 16.38%.

The preparation of dibarium trisilicate required many heats and a long period of time, even though the mixture was strongly pelletized. The records show totals of 11

days at 1050°, 78 hr. at 1200°, 24 hr. at 1250°, and 6 hr. at 1300°. The product gave an X-ray diffraction in excellent agreement with that of Austin.⁶ Chemical analysis showed 63.00% barium oxide, 37.05% silica, and 0.01% iron and aluminum oxides (theoretical analysis, 62.98% barium oxide and 37.02% silica).

The stoichiometric mixture for preparing barium disilicate was pelletized and heated for a total of 100 hr. at 1100° and 30 hr. at 1300°. The X-ray diffraction pattern obtained immediately after the last heat checked that in the ASTM Catalog. However, the pattern changed slowly with time on standing at room temperature, indicating the compound to be unstable. In using this substance in the subsequently reported measurements, it was reheated to 1300° and quenched to room temperature immediately before each run. Chemical analysis gave 56.05% barium oxide and 43.92% silica, as compared with the theoretical 56.06 and 43.94%.

Strontium oxide was prepared from reagent-grade strontium carbonate by first repeatedly boiling in water and filtering and then heating to 1400° until decomposition was essentially complete. Analysis gave 99.75% strontium oxide and less than 0.1% carbon dioxide. The substance was kept in sealed glass bulbs before use in the measurements.

Barium oxide was prepared from reagent-grade barium hydroxide. The latter was dissolved in water and treated with hydrogen peroxide to precipitate hydrated barium peroxide. The precipitate was dried, heated *in vacuo* to 1300° to decompose it to the normal oxide, and sealed in glass bulbs for preservation. Analysis of the product showed 0.15% water, 0.02% silica and 0.05% barium carbonate as impurities.

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 all instances 940.1 g. of the acid was employed. The masses of the silicates, strontium oxide and barium oxide conformed stoichiometrically in each instance with 0.7420 g. of quartz, which was adopted as a basis. The samples were contained in gelatin capsules for dropping from room temperature (measured and correction made to 25°) into the calorimeter. Correction for the capsules was made from separate measurements of the heat of solution of gelatin under the same calorimetric conditions.

The various compounds that were run picked up small amounts of water in handling. In each instance the amount of this water was determined by weight loss on ignition and correction was applied for it.

It was found expedient to mix about 0.1 g. of barium carbonate per capsule with the barium compounds to prevent clumping and therefore to obtain complete reaction with the acid. The heat of reaction of barium carbonate with the acid was determined as -31.5 cal./g. in separate experiments, and proper correction was applied. The heat of reaction of the barium carbonate was between 0.5 and 2% of the total heat evolved, depending upon the substance under study.

The calorimetric apparatus was that described by Torgeson and Sahama¹ with the modifications reported by King.²

Measurements and Results

All values are in terms of the defined calorie (1 cal. = 4.1840 abs. joules). All weighings were reduced to vacuum, and all molecular weights accord with the 1954–55 Report on Atomic Weights.⁷

(7) E. Wichers, THIS JOURNAL, **78**, 3235 (1956).

(1) D. R. Torgeson and Th. G. Sahama, THIS JOURNAL, **70**, 2156 (1948).

(2) E. G. King, *ibid.*, **73**, 656 (1951).

(3) E. T. Carlson and L. S. Wells, *J. Research Natl. Bur. Standards*, **51**, 74 (1953).

(4) H. O'Daniel and L. Tscheischwili, *Z. Krist.*, **104**, 351 (1942).

(5) A. Silverman, H. Insley, G. W. Morey and F. D. Rossini, *Natl. Research Council Bull.* **118**, June, 1949.

(6) A. E. Austin, *J. Am. Ceram. Soc.*, **30**, 218 (1947).

TABLE I
 HEATS OF REACTION (CAL./MOLE)

Reaction	No. of detns.	ΔH	Uncertainty
(1) $\text{SiO}_2(\text{c}, 25^\circ) + 6\text{HF}(\text{sol}, 73.7^\circ) \rightarrow \text{H}_2\text{SiF}_6(\text{sol}, 73.7^\circ) + 2\text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	7	-33,290	80
(2) $\text{SrO}(\text{c}, 25^\circ) + 2\text{HF}(\text{sol}, 73.7^\circ) \rightarrow \text{SrF}_2(\text{p}, 73.7^\circ) + \text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	5	-65,290	80
(3) $2\text{SrO}(\text{c}, 25^\circ) + 4\text{HF}(\text{sol}, 73.7^\circ) \rightarrow 2\text{SrF}_2(\text{p}, 73.7^\circ) + 2\text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	5	-131,070	100
(4) $\text{BaO}(\text{c}, 25^\circ) + 2\text{HF}(\text{sol}, 73.7^\circ) \rightarrow \text{BaF}_2(\text{p}, 73.7^\circ) + \text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	11	-73,040	120
(5) $2\text{BaO}(\text{c}, 25^\circ) + 4\text{HF}(\text{sol}, 73.7^\circ) \rightarrow 2\text{BaF}_2(\text{p}, 73.7^\circ) + 2\text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	11	-146,080	240
(6) $\text{SrSiO}_3(\text{c}, 25^\circ) + 8\text{HF}(\text{sol}, 73.7^\circ) \rightarrow \text{SrF}_2(\text{p}, 73.7^\circ) + \text{H}_2\text{SiF}_6(\text{sol}, 73.7^\circ) + 3\text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	6	-67,340	110
(7) $\text{Sr}_2\text{SiO}_4(\text{c}, 25^\circ) + 10\text{HF}(\text{sol}, 73.7^\circ) \rightarrow 2\text{SrF}_2(\text{p}, 73.7^\circ) + \text{H}_2\text{SiF}_6(\text{sol}, 73.7^\circ) + 4\text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	6	-114,320	200
(8) $\text{BaSiO}_3(\text{c}, 25^\circ) + 8\text{HF}(\text{sol}, 73.7^\circ) \rightarrow \text{BaF}_2(\text{p}, 73.7^\circ) + \text{H}_2\text{SiF}_6(\text{sol}, 73.7^\circ) + 3\text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	6	-68,300	90
(9) $\text{Ba}_2\text{SiO}_4(\text{c}, 25^\circ) + 10\text{HF}(\text{sol}, 73.7^\circ) \rightarrow 2\text{BaF}_2(\text{p}, 73.7^\circ) + \text{H}_2\text{SiF}_6(\text{sol}, 73.7^\circ) + 4\text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	6	-114,890	110
(10) $\text{Ba}_2\text{Si}_2\text{O}_7(\text{c}, 25^\circ) + 22\text{HF}(\text{sol}, 73.7^\circ) \rightarrow 2\text{BaF}_2(\text{p}, 73.7^\circ) + 3\text{H}_2\text{SiF}_6(\text{sol}, 73.7^\circ) + 8\text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	6	-165,530	80
(11) $\text{BaSi}_2\text{O}_7(\text{c}, 25^\circ) + 14\text{HF}(\text{sol}, 73.7^\circ) \rightarrow \text{BaF}_2(\text{p}, 73.7^\circ) + 2\text{H}_2\text{SiF}_6(\text{sol}, 73.7^\circ) + 5\text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	3	-98,340	150

Each heat of formation is the resultant of measurements of a series of reactions for which skeleton equations are given in Table I. The precision uncertainties were calculated according to the methods of Rossini and Deming.⁸

The experimental data are given in Table I which shows the reactions, numbers of determinations, average heat values, and precision uncertainties. In this table, "c" denotes a crystalline substance, "sol" denotes a substance in solution, and "p" denotes a precipitate.

The heat of reaction 1 is from the paper of King,² who employed the same equipment and calorimetric conditions as in the present work.

Each of reactions 2 to 5 were conducted in solutions identical in composition with the final solution from reaction 1. Each of reactions 6 to 11 were conducted in fresh acid, without previous additions. This procedure is necessary to produce the exact material balance in the summation of the reaction heats to obtain the desired heats of formation of the silicates from their constituent oxides.

The heat of reaction 3 is nearly 500 cal. more than twice that of reaction 2, showing that there is a considerable concentration effect. On the other hand, the concentration effect for reactions 4 and 5 was negligible. Eleven determinations were made of the heat of reaction of barium oxide with acid containing the proper amount of dissolved silica. The samples of barium oxide were varied in size to cover the composition range necessary to conform stoichiometrically with compounds ranging from BaSi_2O_7 to Ba_2SiO_4 . No significant dependence of the heat of reaction on sample size was noted, and so the same molal value is used in obtaining the heats of formation of all the barium silicates.

Measurement of the heat of reaction 11 was difficult because of the previously mentioned instability of barium disilicate. Even though the samples were heated to 1300° and quenched to room temperature, the results were uncertain. The three best values obtained are -98,220, -98,470 and -98,330 with a mean of $-98,340 \pm 150$ cal.

Table II illustrates the use of the data in Table I for obtaining heats of formation of the silicates from their constituent oxides.

(8) F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

 TABLE II
 HEAT OF FORMATION OF SrSiO_3 (CAL./MOLE)

Reaction	ΔH	Uncertainty
(1) $\text{SiO}_2(\text{c}, 25^\circ) + 6\text{HF}(\text{sol}, 73.7^\circ) \rightarrow \text{H}_2\text{SiF}_6(\text{sol}, 73.7^\circ) + 2\text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	-33,290	80
(2) $\text{SrO}(\text{c}, 25^\circ) + 2\text{HF}(\text{sol}, 73.7^\circ) \rightarrow \text{SrF}_2(\text{p}, 73.7^\circ) + \text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	-65,290	80
(6) $\text{SrSiO}_3(\text{c}, 25^\circ) + 8\text{HF}(\text{sol}, 73.7^\circ) \rightarrow \text{SrF}_2(\text{p}, 73.7^\circ) + \text{H}_2\text{SiF}_6(\text{sol}, 73.7^\circ) + 3\text{H}_2\text{O}(\text{sol}, 73.7^\circ)$	-67,340	110
(12) $\text{SrO}(\text{c}, 25^\circ) + \text{SiO}_2(\text{c}, 25^\circ) \rightarrow \text{SrSiO}_3(\text{c}, 25^\circ)$ $\Delta H_{12} = \Delta H_1 + \Delta H_2 - \Delta H_6$	-31,240	160

As the final solution after conducting reactions 1 and 2 consecutively in the same acid solution is identical in composition with the solution after conducting reaction 6 in fresh acid, it follows that the reactions and heats may be added as indicated to obtain the heat of formation of strontium metasilicate at 25° from its constituent oxides.

The heats of formation of the crystalline strontium and barium silicates, obtained in this manner, appear in Table III. Because of the before mentioned difficulty of measurement, it is recommended that the value for barium disilicate be interpreted as setting an upper limit (algebraic) to the heat of formation, rather than as clearly defining its value.

TABLE III

HEATS OF FORMATION FROM THE OXIDES (KCAL./MOLE)			
Substance	$\Delta H_{298.15}$	Substance	$\Delta H_{298.15}$
SrSiO_3	-31.24 ± 0.16	Ba_2SiO_4	-64.48 ± 0.28
Sr_2SiO_4	$-59.04 \pm .24$	$\text{Ba}_2\text{Si}_2\text{O}_7$	$-82.42 \pm .35$
BaSiO_3	$-38.03 \pm .17$	BaSi_2O_7	$-41.28 \pm .25$

Related Thermal Data.—The heats of formation of the meta- and orthosilicates of magnesium, calcium, strontium and barium are assembled for comparison in Table IV. The values for the magnesium and calcium compounds are from the work of Torgeson and Sahama¹ and King,² except for $\text{Ca}_2\text{SiO}_7(\gamma)$, which was derived from unpublished data of Coughlin and O'Brien of this Laboratory.

Rossini and co-workers⁹ list values leading to the following heats of formation from the oxides (kcal./mole): -24.7 for strontium metasilicate, -33.0 for strontium orthosilicate, -20.7 for barium metasilicate, and -24.6 for barium orthosilicate, based upon older thermochemical work. The present values are considered much superior. It is of interest to note that the new values become increasingly negative in going from magnesium to barium in both the meta- and ortho-series whereas the solder work indicated a reversal in this trend.

TABLE IV
HEATS OF FORMATION FROM THE OXIDES AT 298.15°K.
(KCAL./MOLE)

Substance	ΔH	Substance	ΔH
MgSiO ₃ ^a	-8.69 ± 0.15	Mg ₂ SiO ₄ ^c	-15.12 ± 0.21
CaSiO ₃ ^b	$-21.25 \pm .13$	Ca ₂ SiO ₄ (β)	$-30.19 \pm .23$
SrSiO ₃	$-31.24 \pm .16$	Ca ₂ SiO ₄ (γ)	-32.7
BaSiO ₃	$-38.03 \pm .17$	Sr ₂ SiO ₄	$-50.04 \pm .24$
		Ba ₂ SiO ₄	$-64.48 \pm .28$

^a Clinoenstatite. ^b Wollastonite. ^c Forsterite.

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. In this connection, the heat of formation of quartz (-210.26 kcal./mole) obtained by

(9) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Natl. Bur. Standards Circular 500, Feb. 1, 1952.

Humphrey and King¹⁰ and the recent value of Huber and Holley¹¹ for calcium oxide (-151.79 kcal./mole) are adopted. Shomate and Huffman¹² and Holley and Huber¹³ have obtained values of the heat of formation of magnesium oxide that differ by only 140 cal./mole; the mean, -143.77 kcal./mole, is adopted. Values for strontium oxide (-141.1 kcal./mole) and barium oxide (-133.4 kcal./mole) are from NBS Circular 500.⁹ These values lead to the heats of formation from the elements listed in Table V, which also brings up-to-

TABLE V
HEATS OF FORMATION FROM THE ELEMENTS AT 298.15°K.
(KCAL./MOLE)

Substance	ΔH	Substance	ΔH
MgSiO ₃	-362.7	SrSiO ₃	-382.6
Mg ₂ SiO ₄	-512.9	Sr ₂ SiO ₄	-542.5
CaSiO ₃	-383.3	BaSi ₂ O ₅	-595.2
Ca ₂ SiO ₄ (β)	-544.0	Ba ₂ Si ₃ O ₈	-980.0
Ca ₂ SiO ₄ (γ)	-546.5	BaSiO ₃	-381.7
Ca ₃ SiO ₅	-692.6	Ba ₂ SiO ₄	-541.5

date the values given by Torgeson and Sahama¹ and King.²

(10) G. L. Humphrey and E. G. King, THIS JOURNAL, **74**, 2041 (1952).

(11) E. J. Huber, Jr., and C. E. Holley, Jr., *J. Phys. Chem.*, **60**, 498 (1956).

(12) C. H. Shomate and E. H. Huffman, THIS JOURNAL, **65**, 1627 (1943).

(13) C. E. Holley, Jr., and E. J. Huber, Jr., *ibid.*, **73**, 5577 (1951). BERKELEY 4, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

Low Temperature Heat Capacities of Magnesium Diboride (MgB₂) and Magnesium Tetraboride (MgB₄)

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The heat capacities of magnesium diboride (MgB₂) and magnesium tetraboride (MgB₄) were measured in the temperature range 18 to 305°K. The values of heat capacity, entropy, enthalpy and free energy function have been tabulated at integral values of temperature. The entropy at 298.16°K. of MgB₂ is 8.60 ± 0.04 cal. deg.⁻¹ mole⁻¹, that of MgB₄ is 12.41 ± 0.06 cal. deg.⁻¹ mole⁻¹. The heat capacity of these compounds at the lowest temperatures measured do not exhibit at T^2 relationship characteristic of some substances having a layer structure.

Introduction

The existence of magnesium borides with formulas MgB₂^{2,3} and MgBr₄² has been shown by X-ray diffraction studies and chemical analysis. The diboride has a layered structure in which hexagonal nets of boron atoms are separated by layers of magnesium atoms. The structure of the tetraboride is not known. Recent studies have shown that in crystalline substances with layer structures, such as graphite⁴ and gallium,⁵ the heat capacity at low temperatures follows a T^2 law, rather than the Debye T^3 law. However, for CdI₄, a compound having a layered structure, it has been found that neither the T^2 nor T^3 relationship was followed

at low temperatures.⁶ The pronounced anisotropy characteristic of the graphite and gallium structures does not prevail in CdI₄ which may account for the lack of a T^2 relationship in the latter case.

The layer structure of MgB₂ is more closely related to that of CdI₄ than that of graphite from the standpoint of anisotropy. However, in the case of MgB₄, if the hexagonal boron network is retained, the interactions between the layers may be sufficiently diminished so as to lead to a T^2 dependence in the heat capacity at relatively low temperatures.

Apparatus and Procedure

Calorimeter.—The Nernst type vacuum calorimeter which was used for the measurements was similar to that described by Johnston and Kerr⁷ with only minor changes being made in the calorimeter assembly and vacuum system.

(1) Department of Chemistry, Ohio State University, Columbus, O.

(2) V. Russell, R. Hirst, F. A. Kanda and A. J. King, *Acta Cryst.*, **6**, 870 (1953).

(3) M. E. Jones and R. E. Marsh, THIS JOURNAL, **76**, 1434 (1954).

(4) W. DeSorbo and W. W. Tyler, *Phys. Rev.*, **83**, 878 (1951); *J. Chem. Phys.*, **21**, 1660 (1953).

(5) W. DeSorbo, *ibid.*, **21**, 168 (1953).

(6) A. S. Dworkin, D. J. Sasmor and E. R. Van Artsdalen, THIS JOURNAL, **77**, 1304 (1955).

(7) H. L. Johnston and E. C. Kerr, *ibid.*, **72**, 4733 (1950).