

Heats of Formation of Xonotlite, Hillebrandite, and Foshagite

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The heats of solution of synthetic xonotlite, $5\text{CaO}\cdot 5\text{SiO}_2\cdot \text{H}_2\text{O}$, hillebrandite, $2\text{CaO}\cdot \text{SiO}_2\cdot \text{H}_2\text{O}$, and a sample of naturally occurring foshagite, $5\text{CaO}\cdot 3\text{SiO}_2\cdot 3\text{H}_2\text{O}$, were determined in a mixture of nitric and hydrofluoric acids, and their heats of formation from the oxides were calculated to be -92.6 , -34.7 , and -94.6 kilocalories per mole, respectively.

1. Introduction

The system $\text{CaO}\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-H}_2\text{O}$ includes the major constituents of portland and high-alumina cements and the reaction products formed by the hydration of these materials. In connection with the hydrothermal study of parts of that system [1,2]¹ being conducted at the National Bureau of Standards, the heats of solution of the reaction products and of related minerals are being determined. The heats of solution of these materials and of the reactants from which they theoretically can be formed are measured in appropriate acid solutions in a precision-type calorimeter. The data, combined with literature values for the heats of formation of the reactants [3], permit the calculation of the heats of formation of substances related to the products of hydration of the cements. Appropriate thermochemical equations can be written and the computed heats of reaction can be compared with observed measurements [4,5] for the further elucidation of the hydration reactions occurring between water and hydraulic cements. The present paper gives the results of measurements made with calcium hydroxide and silica gel as reactants and of synthetic hillebrandite, $2\text{CaO}\cdot \text{SiO}_2\cdot \text{H}_2\text{O}$, and xonotlite, $5\text{CaO}\cdot 5\text{SiO}_2\cdot \text{H}_2\text{O}$, as products. In addition, the heat of solution of a sample of the mineral foshagite was determined.

2. Materials, Apparatus, and Procedure

2.1. Materials

Reagent-quality nitric and hydrofluoric acids, calcium carbonates (low alkali), calcium hydroxide, and precipitated silica (silicic acid) were used. Calcium hydroxide for heat-of-solution measurements was prepared by igniting CaCO_3 for 72 hours at $1,000^\circ\text{C}$ and treating the resulting CaO with water [10] at 250°C for 2 days. The crystals of $\text{Ca}(\text{OH})_2$ obtained were dried, without washing, in a vacuum over magnesium perchlorate and stored in a tightly stoppered bottle in a desiccator over saturated KOH until used. The ignition loss of this material was

24.30, percent, to be compared with 24.31, percent calculated from the formula.

The reagent-quality silicic acid used for the heat-of-solution measurements had a water content of 12.82 percent and a nonvolatile residue of 0.023 percent when treated with hydrofluoric acid. The silica was kept over saturated $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ solution for 2 weeks before its heat of solution was determined. At that time the water content was about 20 percent. According to Mulert [9], whose data were used in calculating the heat of formation of $\text{SiO}_2\text{-aq}$ given in reference [3], the heat of solution of hydrated silicic acid per mole of silica does not change with further increase in water content.

Xonotlite was prepared from $\text{Ca}(\text{OH})_2$ and silicic acid. These materials were mixed together in a CaO/SiO_2 ratio of 1.000 by tumbling for several hours in a glass bottle with a few wooden balls. Twenty grams of this mixture was prepared and heated overnight at 950°C in a platinum dish, cooled in a desiccator and flooded with freshly boiled distilled water. The dish was transferred to a small bomb and heated at 250°C . The flooding and transfer of the dish and the closure of the bomb were made as rapidly as possible to minimize exposure to CO_2 in the air. The bomb was opened at the end of 2 weeks and the hardened mass of surface-dry material ground quickly to pass through a No. 28 sieve and dried for 2 hours in a vacuum over $\text{Mg}(\text{ClO}_4)_2$.

Three samples of synthetic hillebrandite, $\text{C}_2\text{SH}(\text{B})$ [11], were prepared in a similar manner by heating the material with water at 242° , 178° , and 152°C for 7, 16, and 14 days, respectively. These samples also, as well as selected fibers of foshagite from Crestmore, Calif., were crushed rapidly to pass a No. 28 sieve and dried.

The samples were analyzed for SiO_2 , $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$, CaO , and MgO by the methods described in Federal Specification SS-C-158c. Loss on ignition was determined by heating 1-g samples at $1,200^\circ\text{C}$. The CO_2 content was determined on 2-g samples, and the water content was taken as the difference between the loss on ignition and the CO_2 content. X-ray patterns, obtained by using a recording X-ray diffractometer with copper radiation 1.5418 \AA , were used to confirm the identity of the samples by comparison with published patterns [12].

¹ Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. Analysis of calorimeter samples

Determinations	Ca(OH) ₂	SiO ₂ -aq ^a	Xonotlite		Hillebrandite					Foshagite		
			Computed ^b	Observed	Computed ^b	Observed					Computed ^b	Observed
						1	2	3	4	5		
Ignition residue.....	% 75.99	% 87.18	% 96.99	% 96.54	% 90.53	% 67.57	% 69.25	% 89.29	% 29.46	% 91.74	% 99.30	% 88.45
CaO.....	* 75.99		46.86	45.91	66.96	(43.55)	57.52	(57.56)	28.64	60.93	54.46	48.91
SiO ₂		* 87.18	50.10	48.96	31.57	(29.89)	31.56	(31.51)	31.02	31.86	35.01	32.60
CO ₂	9.15			0.27		(1.27)	1.66	(1.68)	0.35	0.64		2.67
H ₂ O ^d	24.16	12.82	3.61	3.19	9.47	(31.16)	9.97	(9.03)	10.17	8.22	10.50	6.68
R ₂ O.....				0.21		(0.09)	0.12	(0.12)	0.14	0.26		0.50
MgO.....				.31					.69			2.61
HF residue.....		0.023										
Analysis, total.....	100.00	100.00	100.00	98.75	100.00	(99.90)	99.95	(99.95)	101.01	100.49	100.00	100.17

^aAs taken from stock bottle. ^bComputed from formula 5CaO·6SiO₂·H₂O for xonotlite; 2CaO·SiO₂·H₂O for hillebrandite; and 5CaO·3SiO₂·3H₂O for foshagite. ^cBy difference. ^dLoss on ignition minus CO₂.

The results of the chemical analyses are given in table 1. For easy comparison there are also included the analyses of the silicates computed from the formulas. The first sample of hillebrandite, prepared considerably before the others, was found to contain excess moisture. It was dried further and analyzed and its heat of solution again measured. Subsequently, its ignition loss and heat of solution were redetermined. This material appears as hillebrandite samples 1, 2, and 3 in the tables. Figures in parentheses in table 1 represent its analysis as sample 2 computed to its moisture content as samples 1 and 3.

The agreement between observed and calculated compositions was satisfactory for the synthetic preparations. The foshagite, however, had undergone considerable alteration. The sample consisted of selected fibers, taken from a 50-g fibrous mass. Perhaps 30 percent of the sample was of somewhat lower index than reported for foshagite, and some brownish material was present.

2.2. Apparatus and Procedure

The calorimeter has been adequately described elsewhere [6, 7]. It was operated so that the final temperature was always within a few hundredths of a degree of 25°C. Since the heat capacities of the reactants were used in computations, the isothermal heats of solution at 25°C were obtained. The energy equivalent of the calorimeter was determined electrically, using the defined calorie of 4.1840 absolute joules. The heat capacities of the samples, introduced at room temperature, were taken as 0.2 cal/deg-g. The calculated correction for the sensible heat introduced with a sample rarely amounted to as much as 0.05 cal/g.

The acid charge used had a total weight of 600.0 g, of which 11.0 ml (12.6 g) was 48 percent HF, the remainder being 2.000 N HNO₃ (at 25°C). Its composition therefore [8] was 0.30HF, 1.10 HNO₃, 29.10H₂O. The sample weight was generally 1 g. When silica gel containing 20 percent of H₂O was being dissolved, the HF/SiO₂ molar ratio was 22.8, well in excess of the value of six, beyond which the

heat of solution of silica in hydrofluoric acid becomes constant [9]. It was observed that 3-g samples of portland cement containing about 1.8 g of combined CaO could be dissolved without precipitation of CaF₂, but that when dissolving Ca(OH)₂ alone the sample weight had to be reduced to 0.7 g. Under these conditions there was no weighable or visible precipitate of CaF₂, but with 0.8-g samples of Ca(OH)₂ a faintly visible haze remained in the solution after filtration had removed 0.6 mg of precipitated CaF₂. Consequently approximately 0.7-g samples of Ca(OH)₂ were used to determine the heat of solution of that substance. It was assumed that the heat of the dilution effects caused by the differences in the concentrations of the final solutions were negligible, and no corrections were made.

3. Results and Discussion

The observed heats of solution are given in table 2. The amount of CaCO₃ equivalent to the CO₂ was calculated for each sample, and its heat of solution, 86 cal/g [4], deducted from the observed heat of solution. The total CaO was reduced by an equivalent amount. The heats of solution of the samples per mole of SiO₂, *A*, were calculated by the formula $A = a(100 \times 60.06/P)$, where *a* is the observed heat of solution of the sample, corrected for CO₂, *P* is the percentage of silica in the sample as given in table 1, and 60.06 is taken as the molecular weight of SiO₂. These calculated values are given in table 3. Empirical formulas, calculated from table 1 corrected for CO₂, are also given in table 3. In making the foregoing calculations for the foshagite, an equivalent amount of CaO was substituted for the MgO found by analysis.

The heat of solution of *C/S*² moles of Ca(OH)₂ was calculated for each sample and added to the heat of solution of 1 mole of SiO₂, 0.828H₂O to determine the heats of solution of the reactants from which the

¹ Conventionally, CaO, SiO₂, and H₂O are represented by the letters C, S, and H, respectively, 2CaO·SiO₂·H₂O being represented by the formula C₂SH.

TABLE 2. Results of calorimetric measurements

Calorimeter energy equivalent	Heats of solution								
	Ca(OH) ₂ ^a	SiO ₂ ·aq ^c	Xonotlite	Effebrandite					Natural forstgite
				1	2	3	4	5	
cal/g ^m 4	cal/g	cal/g	cal/g	cal/g	cal/g	cal/g	cal/g	cal/g	cal/g
5722.2	429.57	468.72	490.87	369.4	462.40	490.62	470.47	480.39	437.94
5730.9	429.69	468.94	490.92	361.0	461.57	490.00	470.22	480.19	438.67
5716.9	429.39	468.81	490.67	-----	461.79	490.53	470.94	480.47	438.66
5718.9	429.31	470.85	491.66	-----	-----	490.46	470.14	480.51	439.31
5717.0	429.29	470.00	490.16	-----	-----	470.98	468.91	480.48	438.67
-----	430.24	468.61	490.42	-----	-----	470.26	469.29	480.30	437.77
Average -5719.2	429.63	468.92	490.78	362.7	461.92	476.66	469.68	480.07	438.42
Std. dev. of avg. 1.2	0.17	0.67	0.21	1.7	0.33	0.22	0.27	0.31	0.29

^a 1-g sample in 600-g HF+HNO₃ mixture (0.30HF, 1.10HNO₃, 28.10H₂O).

^b 0.7-g sample in 600-g HF+HNO₃ mixture (0.30HF, 1.10HNO₃, 28.10H₂O).

^c Sample stored over saturated solution of MgCl₂·6H₂O. Relative humidity 83 percent. Ignition residue of sample 80.11 percent, equivalent to 80.09 percent of SiO₂, 0.92 percent of HF residue, 19.99 percent of H₂O. H/S=0.223.

^d ΔR/ΔT is 0.1010 at 25° C; 5719.2 cal/ohm is approximately 577.8 cal/deg.

^e 1-g sample in 425-g HF+HNO₃ mixture (0.22HF, 0.78HNO₃, 30.61H₂O) in vacuum-flask calorimeter.

^f Standard deviation of average = √[(Σr² - (Σr)²]/n(n-1)).

TABLE 3. Heat of reaction of Ca(OH)₂ and SiO₂·0.83H₂O

Sample	Empirical Formula ^a	Heat of solution ^b		Heat of reaction, ΔH
		Products	Reactants	
Ca(OH) ₂	1.00CaO·1.00H ₂ O	-----	21.86	-----
SiO ₂ ·aq	1.00SiO ₂ ·0.83H ₂ O	-----	35.18	-----
Xonotlite	0.96CaO·1.00SiO ₂ ·0.21H ₂ O	59.06	86.40	-7.34
Effebrandite:				
1	1.86CaO·1.00SiO ₂ ·4.35H ₂ O	88.04	95.09	-7.05
2	1.86CaO·1.00SiO ₂ ·0.98H ₂ O	87.31	95.09	-7.78
3	1.86CaO·1.00SiO ₂ ·0.98H ₂ O	89.82	95.09	-8.27
4	2.01CaO·1.00SiO ₂ ·1.08H ₂ O	90.80	99.24	-8.44
5	2.02CaO·1.00SiO ₂ ·0.98H ₂ O	92.18	99.56	-7.38
		Weighted average		-7.91
Forstgite	1.44CaO·1.00SiO ₂ ·0.61H ₂ O ^d	71.13	81.06	-9.93

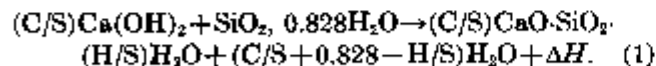
^a Calculated from analysis, corrected for CaCO₃.

^b Corrected for CaCO₃.

^c Kilocalorie per mole of Ca(OH)₂.

^d 2.61 percent of MgO assumed equivalent to 3.83 percent of CaO.

samples can be considered to be formed by the equation



The sum of the heats of solution of the reactants minus the heats of solution of the products is equal to the heat of the reaction. The partial molal heat content of the water in HNO₃, 26.3H₂O is approximately 0.002 kcal/mole; in HF, 100H₂O it is about 0.0004 kcal/mole [13]. These quantities, which represent approximately the heat of solution of the water produced in the reaction, are negligible.

In table 3 are given the calculated heats of reaction of Ca(OH)₂ and silica gel to form the samples used in

this investigation. These values are given on the basis of 1 mole of silica. The hydrated calcium silicates as occurring in nature or as prepared in the laboratory have variable composition. On the assumption that the heats of reaction per mole of silica would be the same for the substances with formulas generally accepted [11], the heats of formation of 5CaO·5SiO₂·H₂O, 2CaO·SiO₂·H₂O, and 5CaO·3SiO₂·3H₂O from lime, quartz, and liquid water were calculated. To perform these calculations, the heat of formation [3] of Ca(OH)₂, SiO₂·aq, and liquid water were substituted in eq (1) together with the heats of reaction as determined from the heat-of-solution measurements. The heats of formation of the hydrated calcium silicates were then obtained as the sum of the heats of formation of the reactants plus the heat of the reaction minus the heat of formation

of the water appearing on the right side of eq (1). Using the heats of formation thus obtained for the silicates, thermochemical equations were written for the reactions forming $5\text{CaO}\cdot 5\text{SiO}_2\cdot \text{H}_2\text{O}$, $2\text{CaO}\cdot \text{SiO}_2\cdot \text{H}_2\text{O}$, and $5\text{CaO}\cdot 3\text{SiO}_2\cdot 3\text{H}_2\text{O}$ from lime, quartz, and liquid water, and the heats of the reactions calculated in the usual manner [3]. The values obtained are given in table 4.

TABLE 4. Heats of formation of hydrated calcium silicates

Name	Bogue designation [11]	Formula *	Heat of formation, ΔH , from $\text{CaO}(s)$, $\text{SiO}_2(s)$, quartz and $\text{H}_2\text{O}(l)$
Xonotlite.....	$\text{C}_5\text{S}_1\text{H}$	$5\text{CaO}\cdot 5\text{SiO}_2\cdot \text{H}_2\text{O}$	kcal/mole -92.6
Hillebrandite..	$\text{C}_2\text{S}_1\text{H}(E)$	$2\text{CaO}\cdot \text{SiO}_2\cdot \text{H}_2\text{O}$	-34.7±0.3
Foshagite.....	$\text{C}_5\text{S}_3\text{H}_3$	$5\text{CaO}\cdot 3\text{SiO}_2\cdot 3\text{H}_2\text{O}$	-94.6

* The heats of formation from the oxides are calculated on the basis of these formulas. The heats of reaction of the reactants $\text{Ca}(\text{OH})_2$ and $\text{SiO}_2(aq)$ to form the individual compounds was taken from table 3 and the heats of formation of the reactants from the oxides calculated from NBS Circular 500 [3].

4. Summary

The heats of solution of synthetic xonotlite, hillebrandite, and natural foshagite have been determined in a mixture of nitric and hydrofluoric acids, and their heats of formation from the oxides have been calculated to be -92.6, -34.7, and -94.6 kcal/mole, respectively.

5. References

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