Heat of Formation of Potassium Calcium Silicate
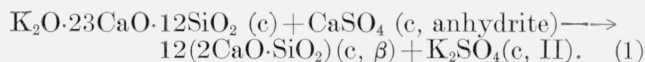
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The heats of solution of $2CaO \cdot SiO_2$ (c, β), $CaSO_4$ (c, anhydrite), K_2SO_4 (c, II) and six members of a series of substitutional solid solutions of K_2O in dicalcium silicate were determined in a nitric-hydrofluoric acid mixture by means of an isothermal-jacket calorimeter. From these data and heats of formation taken from the literature, the heat of formation of $K_2O \cdot 23CaO \cdot 12SiO_2$ (c) was calculated to be $-6,420$ kilocalories per mole at 25° C.

1. Introduction

As part of a continuing investigation of the thermochemical properties of substances occurring in hydraulic cements and their reaction products, the heat of formation of $K_2O \cdot 23CaO \cdot 12SiO_2$, abbreviated $KC_{23}S_{12}$,[1] has been determined. No prior thermochemical data for this compound have been found.

Measurements were made at 25° C of $-\Delta H$, the heat evolved in the reaction

$$K_2O \cdot 23CaO \cdot 12SiO_2 \text{ (c)} + CaSO_4 \text{ (c, anhydrite)} \longrightarrow$$
$$12(2CaO \cdot SiO_2)(c, \beta) + K_2SO_4(c, II). \quad (1)$$

This reaction occurs spontaneously at high temperature [1],[2] where, however, the high-temperature form of $CaSO_4$ is present and liquid K_2SO_4 is formed. The value of $-\Delta H$ was obtained by measuring the heats of solution of these four substances in a mixture of nitric and hydrofluoric acid solutions. The heat of formation of $KC_{23}S_{12}$ at 25° C was calculated from the heat of the reaction and the heats of formation of the other three substances taken from the literature.

2. Materials, Apparatus, and Procedure

Analytical reagents were used in all preparations. Dicalcium silicate, C_2S, was made by the repeated heating at 1,450° C and dusting [3] of a mixture of low-alkali $CaCO_3$ and silicic acid. This material was stablized in the beta form by the addition of about 0.5 percent of B_2O_3 as H_3BO_3 and further heating and grinding. The final product was ground rapidly to pass a No. 100 sieve and stored in a desiccator over magnesium perchlorate and Ascarite.

Potassium sulfate was ground to pass a No. 100 sieve and heated overnight at 220° C. Precipitated gypsum was heated overnight at 1,000° C to convert it to anhydrite. Both of these materials were also stored in the desiccator until tested.

The potassium-containing compound in portland cement clinker, identified by Taylor [2] as $KC_{23}S_{12}$, is now believed to be a solid solution [3] in which K_2O is partially substituted for the CaO in dicalcium silicate. To prepare a series of such solid solutions, six mixtures of $CaCO_3$, silicic acid, and a glass of the composition $K_2O \cdot 4SiO_2$ were heated repeatedly at 1,450° C with intervening grinding. These mixtures were prepared with various amounts of K_2O, the molar ratio of $(CaO + K_2O)/SiO_2$ being maintained at 24/12 (table 1). When microscopical examination indicated that each of these preparations consisted of a single phase, they were rapidly ground to pass a No. 100 sieve and stored in the desiccator until their heats of solution had been determined. The samples were analyzed by the conventional methods for portland cement [4], except that in the determination of SiO_2 in the dicalcium silicate sample, boron was removed by repeated evaporation with methyl alcohol.

The calorimeter and details of its operations have been described previously [5, 6, 7], but a number of minor changes have been made. The heater now consists of a 90-ohm coil of No. 32 double-silk insulated alloy wire in a platinum tube about $\frac{5}{32}$ in. in diameter and 5 in. long. A 4-blade platinum propeller-type stirrer is used in a platinum stirring tube, and the reaction vessel and its cover have been lined with sheet platinum. The heater current, from a bank of storage batteries, is controlled by means of one blade of a 50-amp double-pole double-throw spring toggle switch. Current from a dry cell through the other blade of the switch actuates one pen of a 3-pen tape chronograph. A second pen inscribes a standard seconds signal on the tape which travels at about 1 cm/sec. The maximum timing error probably does not exceed 0.03 sec in 10 min, or 1 part in 20,000. When the switch is in the off position, the heater current is stabilized by discharge through an external resistor. The heater current and voltage, about 0.2 amp and 18 v, respectively, are measured by means of a high-precision potentiometer, a standard 1-ohm resistor, and a volt box. These resistors have been calibrated from time to time by the Electrical Division of the Bureau. Temperature rises are measured with a platinum resistance thermometer, a Mueller G–1 bridge, and a high-sensitivity galvanometer with an optical lever of about 8 m. The apparatus is located in a constant-

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[1] The customary abbreviations C for CaO, K for K_2O, and S for SiO_2 will be used.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] In the absence of stabilizers, the beta form of C_2S inverts to the gamma form at room temperature. The 10-percent increase in volume accompanying this inversion results in the disintegration or "dusting" of the particles into a fine powder. When a stabilizer is added, this dusting does not occur, and grinding is necessary to obtain a powdered material.

TABLE 1. *Analyses of preparations*

	Sample							
	β-C_2S	A	B	C	D	E	F	G[a]
	%	%	%	%	%	%	%	%
SiO_2	34.42	34.54	34.56	34.62	34.34	34.72	34.84	33.99
R_2O_3	0.10	0.28	0.26	0.30	0.12	0.32	0.18	
CaO	65.01	64.42	64.16	63.32	62.46	59.34	60.66	61.14
MgO	.02							
K_2O		0.47	0.93	1.69	2.95	5.65	4.30	4.16
Na_2O		.05	.05	.06	.06	.09	.08	
Total	99.55	99.76	99.96	99.99	99.93	100.12	100.06	99.29
K_2O lost		18	18	25	34	36	35	57
Molar proportions								
CaO	24.27	23.97	23.86	23.51	23.38	21.96	22.38	23.12
K_2O		0.104	0.206	0.373	0.657	1.245	0.944	0.936
SiO_2	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
(K_2O+CaO)		24.07	24.07	23.88	24.04	23.20	23.32	23.05

[a] This sample prepared from K_2CO_3, $CaCO_3$, and silicic acid.

temperature room operated at $25.0 \pm 0.5°$ C during calorimetric measurements. Temperature readings are taken at 2-min intervals during the rating periods and at 1-min intervals during the rapid-rise portion of the experimental period, with integration of the time-temperature curve by application of the trapezoidal rule to the recorded values. The errors introduced in the corrected temperature rise by the departure of this calculated curve from the true indicated time-temperature curve (obtained occasionally by means of the chronograph) are in part compensating and are negligible in comparison with the total error.

In the heat-of-solution determinations, the materials were dissolved in 600.0 g of a mixture of 11 ml of 48-percent HF with 587 g of 2.000 N HNO_3. The weights of the calorimeter samples were calculated according to the stoichiometry of eq (1), based on a sample weight of C_2S of 0.7000 g. This quantity dissolved in 600.0 g of acid solution gave the same sample ratio as the 0.49 g of C_2S dissolved in 420 g of solution, found by Brunauer, Kantro, and Weise [8] to give clear solutions and regular values for the heat of solution. The calculated sample weights were 0.7129, 0.0461, and 0.0590 g for $KC_{23}S_{12}$, calcium sulfate, and potassium sulfate respectively.

In order to make certain that the final calorimeter solutions for the reactants and for the products of eq (1) were identical, both of the reactants were dissolved consecutively in the same solution, the silicate being dissolved first. The same procedure was followed for the products, using a fresh calorimeter charge. Because of the very small heat effects caused by the small samples of $CaSO_4$ and K_2SO_4, the calorimeter was heated to approximately the convergence temperature ($25.17°$ C) before these samples were dissolved, in order to keep the rate of temperature change of the calorimeter as small as possible during the rating periods. The precision of these measurements with small samples was low, since 1-mm deflection on the galvanometer scale corresponded to about 0.04 cal, or about 20 percent of the smallest effect measured. It was thought that the predissolving of 0.7000 g of C_2S (or 0.7129 g of $KC_{23}S_{12}$), corresponding to about 0.008 mole of CaO and 0.004 mol of SiO_2, might have no detectable effect on the heats of solution of the sulfates, since the calorimeter charge consisted of 0.30 mole of HF, 1.10 mole of HNO_3, and 29.10 mole of H_2O. The use of larger samples would result in better precision, although some account might have to be taken of the change of heat of solution with change of sample size. The heats of solution of larger samples, of several sizes, of $CaSO_4$ and K_2SO_4 in the nitric-hydrofluoric acid mixture were therefore determined without previously dissolving the silicates.

The use of standard substances for the calibration of calorimeters is desirable, since thereby the time-temperature curves during calibration and during use are similar. Such a standard substance for the calibration of heat-of-solution calorimeters using the nitric-hydrofluoric acid mixture [4, 9] is heat-treated zinc oxide of analytical reagent quality. For this purpose the zinc oxide is heated at $950°$ C for 1 hr and ground to pass a No. 100 sieve. A weighed sample is reheated for 5 min before use and cooled in a desiccator. The heat of solution of this zinc oxide at $25°$ C is 256.6 cal/g [4, 9]. This value, however, was determined for a ratio of zinc oxide to acid mixture of 7/425, and the resulting temperature rise is about $4.5°$ C. As a useful means of future calibration of such calorimeters for smaller temperature rises, and as a check on the present work, the heat of solution of the standard zinc oxide was determined using samples of 1.56 and 0.20 g in 600.0 g of nitric-hydrofluoric acid mixture in the electrically calibrated calorimeter. The corresponding temperature rises were about 0.7 and $0.09°$ C, respectively.

3. Experimental Results

The compositions of the samples as determined by analysis are given in table 1. It will be seen that from 18 to 36 percent of the K_2O added was lost by volatilization during the preparation of the samples, the percentage loss increasing with increase of K_2O

content. Allowance for the expected loss was made when the samples were proportioned. Six of the completed preparations had ratios of $(CaO+K_2O)/SiO_2$ from 23.88/12 to 24.27/12. The heats of solution of these six samples were used in determining the calculated heats of solution of C_2S and $KC_{23}S_{12}$.

The results of the electrical calibrations and the heat-of-solution measurements are given in tables 2, 3, 4, and 5. The negative sign before values in these tables indicates that the heat of solution was endothermic. The heats of solution of the eight silicate preparations (table 5) are plotted in figure 1 as a function of the percentage of K_2O in the samples. The heats of solution of samples E and F, somewhat deficient in cations, with $(C+K)/S$ ratios of 23.20/12 and 23.32/12, respectively, were less than expected from the values of the other samples. A second-power curve was drawn through the data of figure 1 by the method of least squares, omitting the data for E and F. The average experimental heats of solution of C_2S and sample G, which was close to $KC_{23}S_{12}$ in composition, were 564.8 ± 0.19 and 569.3 ± 0.50 cal/g, respectively (see table 5). The heats of solution of C_2S and $KC_{23}S_{12}$ calculated from the equation of the curve, 565.11 and 568.86 cal/g, respectively, were used to determine $-\Delta H$ of reaction 1. Brunauer, Hayes, and Hass [10] gave the heat of

solution of C_2S as 564.0 ± 2. cal/g, and the value taken from figure 2, p. 774 of the paper by Brunauer, Kantro, and Weise [8] is about 565 cal/g. These values are essentially the same as that obtained for C_2S in the present work.

TABLE 2. *Calibration experiments*

Calorimeter charge, 11 m of 48 percent HF solution and 587 g of 2.000 N HNO₃. Total weight 600.0 g

Electrical calibrations		Heat of solution of zinc oxide at 25° C			
Temperature rise	Electrical energy equivalent	Sample weight	Heat of solution	Sample weight	Heat of solution
Ohms	*cal/Ohm* [a]	*g*	*cal/g*	*g*	*cal/g*
0.069572	5754.1	1.5619	256.82	0.2014	256.8
.069371	5757.0	1.5653	256.88	.2023	257.9
.069489	5759.0	1.5647	257.02	.2021	256.3
.069299	5757.3				
.069214	5761.4				
.069372	5757.4				
Average	[b] 5757.7		256.91		257.0
S.D. [c]	0.98		0.06		0.48
%[d]	.017		.023		.19

[a] 1 cal=4.184 abs j.
[b] dP/dT=0.1010. The energy equivalent is therefore 581.5 cal/deg.
[c] S.D.=standard deviation of the average=$\sqrt{[\Sigma x^2-(\Sigma x)^2/n]/n(n-1)}$.
[d] Coefficient of variation=100×S.D./(average).

TABLE 3. *Heat of solution of* $CaSO_4$ *(anhydrite) in* 600.0 *g of nitric-hydrofluoric acid at 25° C.*

(11 ml of 48% HF and 587 g of 2.000 N HNO₃)

Sample weight	Heat of solution	Sample weight	Heat of solution [b]	Sample weight	Heat of solution [c]	Sample weight	Heat of solution [d]
g	*cal/g*	*g*	*cal/g*	*g*	*cal/g*	*g*	*cal/g*
2.0175	−4.31	0.5091	−4.21	0.1014	−4.69	0.0494	−4.2₃
		.5230	−4.34	.1059	−5.22	.0498	−2.9₉
1.0450	[a]−4.30	.5049	−4.59	.1100	−5.29	.0487	−4.8₄
1.0129	−4.14	.5016	−4.06	.1082	−4.42	.0485	−2.0₄
1.0017	−4.24	.5099	−4.56	.1046	−4.19	.0449	−7.1₅
1.0024	−4.13	.5079	−4.58	.1073	−5.48		
1.0185	−4.17	.5096	−4.28	.1029	−5.09	Average	4.25
		.5043	−4.17			S.D.	0.90
		.5098	−4.26			V, %	21
		.5150	−4.21				

[a] Five 1-g samples dissolved consecutively in a single calorimeter charge.
[b] Ten 1/2-g samples dissolved consecutively in a single calorimeter charge.
[c] Seven 0.1-g samples dissolved consecutively in a single calorimeter charge.
[d] 0.71 g of $K_2O\cdot23CaO\cdot12SiO_2$ predissolved for each determination.

TABLE 4. *Heat of solution of* K_2SO_4 *(c, 11) in* 600.0 *g of nitric-hydrofluoric acid at 25° C.*

(11 ml of 48% HF and 587 g of 2.000 N HNO₃)

Sample weight	Heat of solution	Sample weight	Heat of solution [a]	Sample weight	Heat of solution [a]	Sample weight	Heat of solution [a]
g	*cal/g*	*g*	*cal/g*	*g*	*cal/g*	*g*	*cal/g*
2.0708	−43.56	0.1076	−44.89	0.1038	−43.66	0.0609	−40.5
1.0265	−43.65	.1063	−44.23	.1016	−43.05	.0612	−41.5
0.5109	−44.40	.1079	−44.64	.1095	−41.26	.0603	−41.7
				.1028	−43.90	.0575	−42.2
				.1073	−43.60	.0595	−43.4
						.0600	−43.5
		Average	−44.59		−43.09		−42.6
		S.D.	0.19		0.48		0.25
		V, %	0.43		1.1		0.59

[a] 0.70 g $2CaO\cdot SiO_2$ predissolved for each determination.

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TABLE 5. *Heat of solution at 25° C. of 2CaO·SiO₂ (c, β) and K₂O–CaO–SiO₂ solid solutions in 600.0 g of nitric-hydrofluoric acid*

(11 ml of 48% HF and 587 g of 2.000 N HNO₃)

β−2CaO·SiO₂[a]		A		B		C	
Sample weight	Heat of solution	Sample weight	Heat of solution	Sample weight	Heat of solution	Sample weight	Heat of solution
g	*cal/g*	*g*	*cal/g*	*g*	*cal/g*	*g*	*cal/g*
0.7001	565.3	0.7315	566.2	0.7131	568.8	0.7231	568.3
.7013	565.1	.7013	567.0	.7200	568.4	.7300	567.3
.7080	564.3	.7071	565.9	.7121	567.3	.7227	566.4
.7013	564.9	.7110	565.4	.7105	568.2	.7216	569.4
.7031	564.0	.7065	566.6	.7106	568.0	.7217	568.3
.7066	564.9					.7218	568.7
.6960	565.6					.7205	569.1
.7025	564.4						
Average____	564.8		566.2		568.1		568.2
S.D_____	0.19		0.28		0.25		0.40
V, %_____	0.034		0.049		0.044		0.070

D		E		F		G	
0.7466	568.3	0.7969	567.1	0.7714	568.0	0.7143	568.0
.7497	565.0	.7930	566.7	.7760	568.2	.7169	568.4
.7475	568.4	.7888	565.1	.7680	567.4	.7158	569.0
.7440	568.7	.7985	566.1	.7671	569.5	.7125	566.8
.7450	570.2	.7923	566.2	.7698	567.9	.7087	568.5
.7433	568.5	.7950	567.3	.7663	568.8	.7410	570.3
.7442	568.9	.7942	568.3	.7672	568.1	.7468	569.9
						.7407	572.6
						.7401	570.1
						.7461	569.2
Average____	568.3		566.7		568.3		569.3
S.D_____	0.60		0.38		0.26		0.50
V, %_____	0.11		0.067		0.046		0.088

[a] Weighed in platinum crucible, heated 3½ hr at 1,050° C, cooled in a desiccator, and reweighed before introduction.
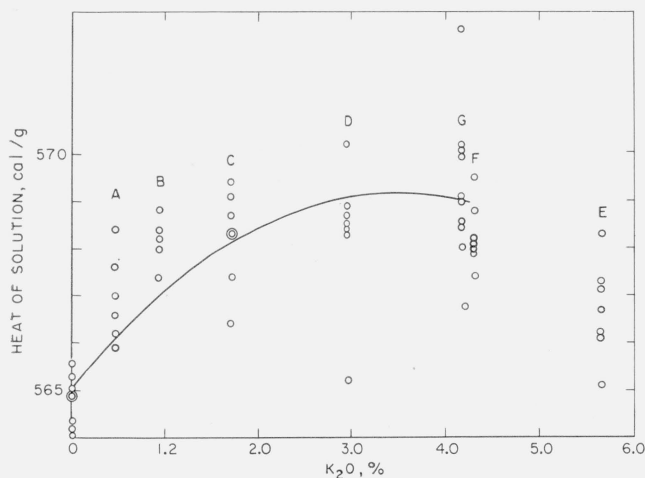

FIGURE 1. *Heats of solution of potassium-calcium-silica solid solutions.*

The heat of solution of CaSO₄ (table 3) does not seem to be significantly affected by sample size or by the presence of predissolved KC₂₃S₁₂. However, the average value −4.25 ± 0.90 cal/g obtained using the 0.049-g samples was used in calculation. The standard deviation was large, as was expected for small samples, but the average value is about the same as determined for larger samples without predissolving the silicate. The experimental values are substantially different than the calculated [11] heat of solution of CaSO₄ in water to form CaSO₄, 100000H₂O (0.045 g CaSO₄/600 g H₂O). +30.1 cal/g, or the value calculated by Brunauer et al.

[10] for the heat of solution in nitric-hydrofluoric acid, +31.2 cal/g [10].

The endothermic heat of solution of K₂SO₄ seemed to increase slightly with decrease in sample size (table 4). The presence of predissolved C₂S also seemed to have a slight effect which a *t*-test [12] showed to be significant at the 5-percent level (comparing the two sets of measurements made with 0.1 g samples, $t=2.65$, $t_{crit.}=2.447$). For the calculation of −ΔH of reaction 1, the value −42.6 ± 0.25 cal/g obtained with 0.06-g samples was used for the heat of solution of potassium sulfate. The calculated value of the heat of solution of K₂SO₄ in water to form K₂SO₄. 1000000 H₂O (0.058 g K₂SO₄/600 g H₂O) is −32.9 cal/g [11].

The standard value of 256.6 cal/g for the heat of solution of zinc oxide in the nitric-hydrofluoric acid mixture at 25°C [4,9] was obtained as the result of tests made with the present calorimeter (using a shorter galvanometer-scale distance) [13] combined with the measurements of Stenzel and Morris [14] at 30° C. The values 257.0 ± 0.48 and 256.91 ± .06 cal/g given in table 2 for ZnO/solution ratios of 0.2/600 and 1.58/600, respectively, agree well with the standard value for which the calculated ratio is 9.88/600. These three values of the heat of solution of zinc oxide lie very close to the line $y=257.0 −23.5\ x$, where y is the heat of solution of zinc oxide in calories per gram, and x is the zinc-oxide per solution weight ratio. Values calculated from this equation can safely be used to calibrate the calorimeter for temperature rises smaller than the 4.5° for which the standard value is given.

4. Heats of Formation

The heat of reaction (ΔH) of eq (1) at 25° C is calculated to be -36.3 ± 1.4 kcal, using the heats of solution given in section 3 and the 1952 atomic weights [15]. The heats of formation of $2CaO \cdot SiO_2(c,\beta)$, $CaSO_4$ (c, anhydrite), and $K_2SO_4(c,\text{II})$ are -538.0, -342.42, and -342.66 kcal/mole respectively, at 25° C [11]. The heat of formation of $K_2O \cdot 23CaO \cdot 12SiO_2(c)$, therefore, is -6420 kcal/mole.

5. Summary

The heats of solution of $2CaO \cdot SiO_2(c,\beta)$, $K_2SO_4(c,\text{II})$, and $K_2O \cdot 23CaO \cdot 12SiO_2(c)$ were determined in a mixture of 2.000 N nitric acid and 48-percent hydrofluoric acid in an isothermal-jacket calorimeter. From these and other data in the literature, the heat of formation of $K_2O \cdot 23CaO \cdot 12SiO_2(c)$ from the elements was calculated to be -6420 kcal/mole at 25° C.

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6. References

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