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Heat of Formation of Calcium Aluminate Tricarbonate at 25 °C

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The heat of formation at 25 °C, $\Delta H_f^\circ = -16{,}228$ kJ/mole, of calcium aluminate tricarbonate, $3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 30H_2O$ (c), was determined by the heat-of-solution method, with $2N$ HCl as the solvent, and $3CaO \cdot Al_2O_3 \cdot 6H_2O$ (c) and $CaCO_3$ (c) as the reactants. The heat of solution in $2N$ HCl is -501.0 kJ/mole, and the heat of the reaction $3CaO \cdot Al_2O_3 \cdot 6H_2O$ (c) + $3CaCO_3$ (c) + $24H_2O$ (l) $\rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 30H_2O$ (c) is -186.6 kJ. The rate at which the heat of solution in $2N$ HCl changes with H_2O content at the $30H_2O$ level, $d(\Delta H)/dn$, is $+9.0$ kJ/mole per mole H_2O. Heats of solution were determined for samples in the range of 6 to $31H_2O$, but decomposition appears to occur on drying to H_2O contents lower than $26H_2O$. The heats of stepwise reactions leading to the formation of calcium aluminate mono- and tricarbonate have also been calculated.

1. Introduction

Hydrated calcium aluminate tricarbonate, $3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 30H_2O$, is a member of a series of complex salts represented by the general formula $3CaO \cdot Al_2O_3 \cdot 3CaX \cdot nH_2O$, in which X is a divalent anion or two units of a monovalent anion, and n is 30 to 32. This series is often referred to as the "high-form" series of complex calcium aluminates; its members generally crystallize as fine hexagonal or pseudohexagonal needles. The tricarbonate is related to calcium aluminate monocarbonate, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$, which is the corresponding member of another series, known as the "low-form" series.

The tricarbonate was first made by Bessey, as reported by Jones [1] [1] and more recently described by Bessey [2], and was also prepared by Carlson and Berman [3]. Bessey reported a compound containing $27H_2O$; Carlson and Berman, $32H_2O$.

As part of a continuing investigation of the thermochemical properties of substances occurring in or related to hydraulic cements and their reaction products, the heat of formation of hydrated calcium aluminate tricarbonate was determined.

Measurements by the heat-of-solution method were made of the heat evolved at 25 °C in the reaction

$$3CaO \cdot Al_2O_3 \cdot 6H_2O(c) + 3CaCO_3(c) + 24H_2O(l) \xrightarrow{\Delta H_1} 3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 30H_2O(c). \qquad (1)$$

The heat of this reaction is the difference between the sum of the heats of solution of the reactants and the heat of solution of the product, in accordance with the following equations:

$$3CaO \cdot Al_2O_3 \cdot 6H_2O(c) + 1623.305(HCl \cdot 26.614H_2O)(aq) \xrightarrow{\Delta H_2} 3CaCl_2(aq) + 2AlCl_3(aq) + 1611.305(HCl \cdot 26.820H_2O)(aq) \qquad (2)$$

$$3CaCO_3(c) + 3CaCl_2(aq) + 2AlCl_3(aq) + 1611.305(HCl \cdot 26.820H_2O)(aq) \xrightarrow{\Delta H_3} 6CaCl_2(aq) + 2AlCl_3(aq) + 3CO_2(aq) + 1605.305(HCl \cdot 26.922H_2O)(aq) \qquad (3)$$

$$24H_2O(l) + 6CaCl_2(aq) + 2AlCl_3(aq) + 3CO_2(aq) + 1605.305(HCl \cdot 26.922H_2O)(aq) \xrightarrow{\Delta H_4} 6CaCl_2(aq) + 2AlCl_3(aq) + 3CO_2(aq) + 1605.305(HCl \cdot 26.937H_2O)(aq) \qquad (4)$$

$$3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 30H_2O(c) + 1623.305(HCl \cdot 26.614H_2O)(aq) \xrightarrow{\Delta H_5} 6CaCl_2(aq) + 2AlCl_3(aq) + 3CO_2(aq) + 1605.305(HCl \cdot 26.937H_2O)(aq). \qquad (5)$$

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

The summation: equation 2 + equation 3 + equation 4 − equation 5 results in equation 1. Similar summation of the ΔH values results in ΔH_1.

The heat of solution of each of the reactants was measured in $HCl \cdot 26.61H_2O$ ($2.00N$ HCl at 25 °C). The heats of formation of the reactants were taken from Circular 500 [4] of the National Bureau of Standards.

All calculations in this paper are based on the 1961 atomic weights [5], and the results are expressed in absolute joules. Data reported in earlier work on the complex calcium aluminates [6, 7, 8], expressed in thermochemical calories, may be converted to joules by multiplying by 4.184. A summary of data so converted is included in this paper.

2. Preparation and Analysis of Samples

2.1. Preparation

Calcium aluminate tricarbonate was formed as a white precipitate by the addition of sodium carbonate solution to a mixture of calcium saccharate and either monocalcium aluminate or potassium aluminate solutions. Calcium saccharate is a solution of CaO in aqueous sucrose, which contains considerably more dissolved calcium than ordinary calcium hydroxide solution. A metastable solution of monocalcium aluminate, containing about 2 g of Al_2O_3 and 1 g of CaO per liter (approximately $0.02M$), was prepared by shaking high-alumina cement with distilled H_2O about 3 hr and quickly filtering. Potassium aluminate solution was prepared by the method of Rabot and Mounier [9].

Four preparations of calcium aluminate tricarbonate were made, two of which provided useful thermochemical data. Details of the preparations are given in table 1.

Preparation 1 was made with calcium saccharate solution which was $0.307M$ with respect to CaO and contained 150 g of sucrose per liter. To 1750 ml of this solution 2500 ml of monocalcium aluminate solution was added, followed by 167 ml of $0.472M$ sodium carbonate solution. The CO_2/Al_2O_3 molar ratio was slightly more than 3:1. No precipitate formed at this point, but precipitation began after the addition of 2 liters of $0.02M$ $Ca(OH)_2$ and 100 ml of $0.44M$ NaOH. The crystals were filtered after standing 2 months.

Preparation 2 was made by adding 283 ml of potassium aluminate solution ($0.204M$ Al_2O_3) to 2 liters of calcium saccharate solution ($0.304M$ CaO), followed by 359 ml of $0.48M$ sodium carbonate solution (CO_2/Al_2O_3 molar ratio of 3:1). Precipitation began after further addition of 3 liters of CO_2-free distilled H_2O, which decreased the sucrose concentration to 50 g per liter. The crystals were filtered after 7 days.

Preparations 3 and 4 were made in the same manner as preparation 2 with slight differences in the concentrations and quantities of the potassium aluminate solutions, somewhat higher Al_2O_3/CaO ratios to obtain a larger quantity of precipitate, but the same CO_2/Al_2O_3 ratio as for preparations 1 and 2. In preparation 4 the calcium saccharate solution was diluted before, rather than after, the addition of the other solutions.

TABLE 1. *Properties of the preparations of calcium aluminate tricarbonate as originally dried at 79 percent relative humidity*

Preparation	1			2			3			4		
		No. of determinations	Std. error		No. of determinations	Std. error		No. of determinations	Std. error		No. of determinations	Std. error
Composition, weight percent:												
CaO [a]	29.09	6	[a] 0.03_4	28.05	4	[a] 0.02_8	27.73	5	[a] 0.04_0	27.00	8	[a] 0.02_6
Al_2O_3 [a]	8.94	4	[a] $.02_7$	8.45	2	[a] $.02_6$	8.11	6	[a] $.00_7$	7.91	8	[a] $.01_8$
Loss on ignition [a]	62.03	2	[a] $.00_6$	63.55	2	[a] $.05_0$	64.09	2	[a] $.00_8$	65.01	2	[a] $.06_9$
CO_2, by acid attack [a]	11.16	2	[a] $.00_5$	10.94	2	[a] $.00_2$	10.46	3	[a] $.01_0$	10.54	2	[a] $.00_2$
CO_2, by ignition [a]	21.38	2	[a] .52	21.96	3	[a] .27	24.87	4	[a] .73	29.70	3	[a] .67
Sucrose [b]	6.48	--------	[b] .34	7.13	--------	[b] .18	9.34	--------	[b] .47	12.42	--------	[b] .43
H_2O [b]	44.38	--------	[b] .34	45.48	--------	[b] .18	44.29	--------	[b] .47	42.05	--------	[b] .44
Molar ratios:												
$CaO:Al_2O_3$ [b]	5.92_3	--------	[b] $.01_9$	6.03_6	--------	[b] $.02_0$	6.21_4	--------	[b] $.01_1$	6.20_5	--------	[b] $.01_5$
$CO_2:Al_2O_3$ [b]	2.89_4	--------	[b] $.00_9$	3.00_0	--------	[b] $.00_9$	2.98_7	--------	[b] $.00_4$	3.08_7	--------	[b] $.00_7$
$H_2O:Al_2O_3$ [b]	28.11_1	--------	[b] .23	30.46_7	--------	[b] .15	30.89_4	--------	[b] .33	30.07_7	--------	[b] .32
Sucrose: Al_2O_3 [b]	0.21_6	--------	[b] $.01_1$	0.25_1	--------	[b] $.00_6$	0.34_3	--------	[b] $.01_7$	0.46_8	--------	[b] $.01_6$
Molar ratios of compounds present, to Al_2O_3:												
$3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot nH_2O$ [b]	$.96_5$	--------	[b] $.00_3$	1.000	--------	[b] .000	$.99_6$	--------	[b] $.00_1$	1.000	--------	[b] .000
where n=	28.68_0	--------	[b] .22	30.43_1	--------	[b] .15	30.76_7	--------	[b] .39	29.95_9	--------	[b] .32
$3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$ [b]	0.03_4	--------	[b] $.00_2$	--------	--------	--------	--------	--------	--------	--------	--------	--------
$Ca(OH)_2$ [b]	--------	--------	--------	0.03_6	--------	[b] $.00_7$	0.24_0	--------	[b] $.01_1$	0.11_8	--------	[b] $.00_9$
$CaCO_3$ [b]	--------	--------	--------	--------	--------	--------	--------	--------	--------	$.08_7$	--------	[b] $.00_7$
$Al_2O_3 \cdot 3H_2O$ [b]	$.00_{15}$	--------	[b] $.00_{35}$	--------	--------	--------	$.00_4$	--------	[b] $.00_1$	--------	--------	--------
Sucrose [b]	$.21_6$	--------	[b] $.01_1$	$.25_1$	--------	[b] $.00_6$	$.34_3$	--------	[b] $.01_7$	$.46_8$	--------	[b] $.01_6$
Heat of solution of the preparation, ΔH J/g [a]	-430.3_2	4	[a] $.5_5$	-425.4_7	2	[a] $.3_6$	-414.1_9	3	[a] $.3_1$	-402.6_8	6	[a] 1.2
Corrected heat of solution of the $3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot nH_2O$ [b]												
ΔH J/g	-450.7_4	--------	--------	-456.7_2	--------	--------	-438.0_7	--------	--------	-453.7_5	--------	--------
kJ/mole	-490.0_1	--------	--------	-510.9_3	--------	--------	-492.8_5	--------	[b] 1.5	-503.7_5	--------	[b] 1.7

[a] Independently determined quantities. Standard errors calculated from replicate determinations.

[b] Derived quantities. Standard error of each derived quantity calculated directly from the standard errors of the applicable independently determined quantities. The independent quantities were used in these calculations to more places than shown in this table.

Preparations 3 and 4 were filtered after 7 and 8 months, respectively. Preparation 3 was washed on the filter with a 50-g/l sucrose solution to remove any excess CaO, and with absolute ethyl alcohol to remove the sucrose solution. Preparations 1, 2, and 4 were not washed, but were sucked "dry" on the filter.

The use of CaO-sucrose solutions appeared to be the only means of making the tricarbonate at room temperature, although Bessey made his early preparation without sucrose by adding ammonium carbonate solution slowly to calcium aluminate solution at low concentration with rapid stirring. It might be possible to prepare the compound at subfreezing temperatures without sucrose if an analogy with the calcium aluminate chlorides is valid; this possibility has not been investigated.

Preparation of the reagents, transfer of solutions, mixing, filtration, and other operations were performed in closed systems with precautions taken to exclude CO_2. All solutions were made with distilled water which had been boiled and then cooled in a current of CO_2-free air.

The filtered preparations were dried at 79 percent relative humidity in a desiccator over saturated NH_4Cl [10]. When the loss on ignition of a preparation had become constant, the material was ground and mixed in a sealed jar containing wood balls, and the ground material was returned to the desiccator for storage. Before placing the samples in the desiccators and after opening them at any time, the desiccators were evacuated to 2 to 4 cm Hg pressure and refilled with CO_2-free air which had been passed through a gas-washing bottle containing the same solution as in the desiccator. A detailed description of this technique may be found in reference [11].

The dried, ground samples were analyzed chemically to determine their composition. Heat-of-solution determinations were then made. The remaining portions of the preparations were subjected to further drying over the following desiccants: saturated $MgCl_2 \cdot 6H_2O$ (33% relative humidity) (which produced an insignificant loss of H_2O), saturated LiCl (12% relative humidity) [10], 20*N* H_2SO_4 (10% relative humidity), 23*N* H_2SO_4 (5% relative humidity) [12], and CaO (0% relative humidity). The heat of solution of these dried samples was determined at various stages of the drying process.

2.2. Chemical Analysis

Unlike other representatives of the complex calcium aluminate family prepared earlier [6, 7, 8], which had attained a maximum purity of 99 percent by weight, the preparations of calcium aluminate tricarbonate were only 87 to 92 percent pure. The major impurity was sucrose. This compound interferes with the usual method of determining H_2O content, which has been to ignite a sample at 1200 °C and subtract the separately determined CO_2 content from the loss on ignition. It interferes as well with the determination of Al_2O_3 and CaO by the classical precipitation methods.

The sucrose content was determined from the difference between the total CO_2 obtained by combustion of the sample in oxygen and the carbonate CO_2 obtained by dissolving the sample in dilute hydrochloric acid. This method was more accurate than attempts to determine sucrose by solubility in water or alcohol or by oxidimetric methods. Nevertheless, it proved to be the weakest link in the precision calculations. Inasmuch as the H_2O was determined as (ignition loss—carbonate CO_2—sucrose), the relatively poor precision of the sucrose determinations is reflected in the standard errors of the H_2O percentages and H_2O content of the preparations, table 1.[2] Fortunately, the sucrose had only a minor effect on the corrected heats of solution.

However, as shown in table 1, considerably better precision was obtained in the determination of CaO, Al_2O_3, and carbonate CO_2. The CaO and Al_2O_3 were determined by the referee methods of Federal Test Method Standard 158a [13], except that the dry sample was first ignited to destroy the sucrose, then dissolved in HCl. To conserve material, some determinations of Al_2O_3 and CaO were made from the solution remaining after a carbonate-CO_2 determination. In these instances the following technique was used to destroy the sucrose in the solution: The solution was evaporated on a steam bath to dryness, acidified with HCl, diluted with hot water, and filtered to remove any silica present (derived from decomposition of silicone grease used in the glass seals of the CO_2-evolution apparatus). The paper and precipitate were burned and ignited at about 600 °C, and any SiO_2 then volatilized with H_2SO_4 and HF. The filtrate was transferred by stages into the crucible containing the HF residue, and evaporated to dryness; the evaporation was completed in a 100° oven and the temperature then gradually raised in a furnace to 700 °C. The sucrose was thereby destroyed and the samples were ready for analysis after solution in HCl.

The oxide analyses and sucrose contents of the preparations are given in table 1. As pointed out in reference [8], the estimates of standard error for each determination were calculated separately for each preparation, rather than by pooling the standard error estimates for that particular determination for all preparations. This procedure is based on the assumption that, for a particular preparation, the precision of the analysis is dependent in part on the uniformity of the preparation and not simply on the degree to which an analytical method can be reproduced. The estimated uncertainty of the mole ratios of the compounds assumed to be present as impurities is an indication of the quantitative reliability of the impurity calculations. The method used for estimating this uncertainty is given in an appendix to this paper.

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[2]

$$\text{Standard error} = \sqrt{\frac{\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n}}{n(n-1)}}$$

where x_i is the result obtained for one measurement and n is the number o measurements.

TABLE 2. *X-ray diffraction patterns of calcium aluminate tricarbonate preparations*

Preparation 1		Preparation 2		Preparation 3		Preparation 4		C&B preparation [3]	
d,Å	Intensity [a]	*d*,Å	Intensity [a]	*d*,Å	Intensity [a]	*d*,Å	Intensity [a]	*d*,Å	Relative intensity
9.34	>100	9.40	>100	9.60	>100	9.71	>100	9.41	100
5.42	29	5.43	37	5.47	36	5.50	32	5.43	27
								5.31	4
4.82	28	4.84	35	4.87	24	4.90	20	4.83	20
4.62	35	4.62	34	4.65	24	4.68	21	4.62	26
		4.13	19						
3.79	52	3.79	42	3.81	52	3.83	38	3.80	42
3.52	27	3.52	22	3.53	25	3.56	13	3.52	20
3.37	35	3.37	40	3.39	38	3.41	28	3.37	27
3.13	7	3.14	8	3.15	8	3.17	7	3.13	4
3.036	9			3.06	34	3.06	5		
2.962	9	2.98	10	2.98	10	2.99	7	2.962	8
2.697	42	2.70	49	2.71	48	2.72	36	2.700	35
2.654	7	2.66	7	2.66	10	2.67	6	2.653	11
2.627	2	2.62	7	2.62	9	2.63	5		
2.603	3							2.605	5
2.527	[b] 22							2.529	7
2.505	84	2.51	77	2.520	88	2.52	65	2.507	67
								2.466	3
2.413	3	2.42	5	2.43	7	2.43	5	2.413	4
2.339	4	2.34	9	2.35	7	2.36	6	2.339	6
				2.32	6	2.32	4	2.310	4
2.255	3								
2.151	37	2.15	39	2.16	46	2.17	32	2.156	37
2.093	21	2.10	23	2.11	26	2.11	18	2.098	19
								2.049	3
1.997	6	2.00	9	2.00	9	2.01	6	1.996	5
1.976	3							1.977	3
1.912	8	1.916	11	1.92	8	1.93	8	1.913	7
1.878	13	1.883	18	1.89	18	1.89	12	1.879	12
1.823	5	1.826	10	1.83	12	1.83	9	1.822	9
[c] 1.786	5								
1.770	7	[c] 1.773	9	[c] 1.773	7	[c] 1.78	7	1.768	7
								1.758	2
								1.739	2
1.711	2					1.72	2	1.711	2
1.685	3	1.691	5	1.694	3	1.69	3	1.684	4
		1.674	3	1.677	3	1.68	3		
1.646	5	1.652	5	1.654	7	1.66	4	1.646	4
1.622	8	1.627	9	1.630	11	1.63	7	1.622	7
1.584	1	1.572	4					1.582	2
								1.568	2
								1.541	2
1.532	4	1.536	6					1.532	4
1.483	3	1.485	6					1.483	5
1.476	2							1.465	3

[a] Intensity for preparations 1, 2, 3, and 4 was measured from actual peak heights on the x-ray diffraction patterns, after subtracting the background level. The intensities for the first peak on each pattern were estimated to be 140 to 165.

[b] Shoulder on large peak; true intensity may be smaller.

[c] Broad peak, centering on *d*-spacing given.

2.3. Characterization

X-ray patterns of the preparations, summarized in table 2, were obtained by the powder method on a Geiger-counter diffractometer with copper Kα radiation. The *d*-spacings are essentially the same as those of the tricarbonate reported in reference [3], also shown in the table, except that a line at 3.035 Å, due possibly to free $CaCO_3$, is present in preparations 1, 3, and 4. Chemical analysis, however, suggests the presence of free $CaCO_3$ only in preparation 4; it is possible that calcium hydroxide or tetracalcium aluminate present in preparations 1 and 3 may have undergone partial carbonation while in the X-ray diffractometer. Other differences among the patterns probably represent small differences of diagram interpretation rather than real variation.

Microscopical examination showed the preparations to be almost entirely clumps of needlelike crystals of negative elongation with refractive indices $\omega=1.490$, $\epsilon=1.480$, both accurate to within 0.003 (ϵ slightly lower in some cases).

Differential thermal analysis (fig. 1) showed a large endothermic area peaking at 145 to 165 °C, due to H_2O loss; a large exothermic area with two peaks at 400 and 465°, presumably due to the oxidation of sucrose; a small exothermic peak at 730 to 800°; and a small endothermic area centering at 860 to 925°, presumably due to evolution of CO_2. The exothermic peak at 390° reported by Carlson and Berman [3], unexplained at that time, is probably an indication that sucrose was present in their preparation, considerably less sucrose, however, than in the preparations reported here. If the presence of sucrose in these preparations had been neglected and its weight included in the H_2O content, the formula reported would have been $3CaO{\cdot}Al_2O_3{\cdot}3CaCO_3{\cdot}38H_2O$ instead of . . . $\cdot 30H_2O$. Although quantitative analytical data cannot be deduced from DTA patterns made four years apart, it can be concluded roughly from the relative areas of the exotherms and endotherms in each pattern that a correction for the sucrose content of Carlson and Berman's preparation would have brought its H_2O content closer to $30H_2O$ than to the $32H_2O$

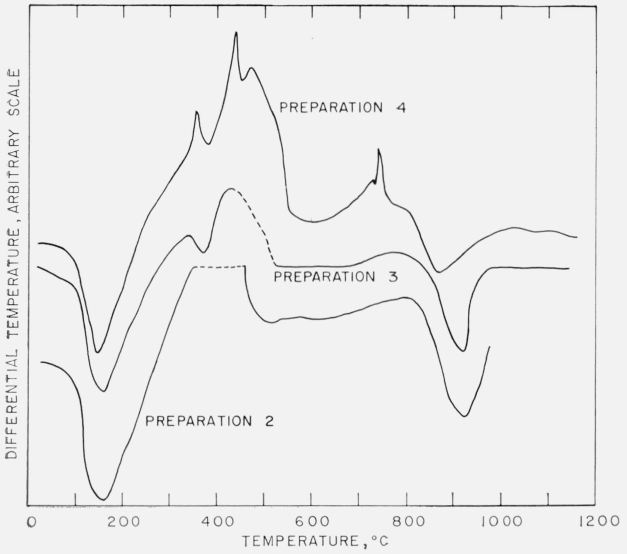

FIGURE 1. *Differential thermal analysis of preparations of calcium aluminate tricarbonate.*

Dashed lines indicate temperature differences which were off-scale (preparation 2) or estimated (preparation 3)

reported. The higher temperature found for the first endothermic peak in the current preparations (165°) than in the preparation of reference [3] can probably be attributed to their greater sucrose content.

Curves of weight loss versus temperature (fig. 2), determined by stepwise heating at a constant temperature to constant weight for each step, showed the greatest slope at low temperatures and leveled off to a minimum slope at about 350 °C. The slope then increased to another maximum between 600 and 700° and leveled off again at about 750° with small weight losses continuing up to 1200°. The first rapid weight loss below 350° represents evolution of water by a combination of dehydration of the tricarbonate and decomposition of the sucrose (a sample of pure sucrose was completely carbonized at 200°); the second, between 500 and 750°, represents loss of residual H_2O and CO_2. In this static thermogravimetric procedure, the changes took place at lower temperatures than in the dynamic DTA determination because the sample remained at a given temperature long enough to reach equilibrium.

3. Heat-of-Solution Measurements

Heats of solution were determined in $HCl\cdot 26.61_4H_2O$ ($2.00N$ HCl at 25 °C). The all-platinum calorimeter described in reference [7] was used, with some modifications to be described below.

As pointed out in the same reference, determination of the heat of solution of carbonates in acids introduces the problem of CO_2 evolution. On dissolving, the sample first releases a large quantity of heat and the temperature rises rapidly, but as CO_2 gas is released from solution endothermically, the temperature in the calorimeter falls (after correction for the temperature rise produced by stirring and leakage of heat from the water bath). This effect takes place even when the CO_2 available is not enough to saturate the acid, as reported in reference [7]. For this reason, it appears uncertain to the author whether the problem can really be solved by using HCl saturated with CO_2 at the start. The loss of heat due to gas evolution makes it difficult to obtain a final rating period in the calorimeter during which no reaction is taking place and the energy of stirring and heat leakage can be measured. If the escape of gas is too violent, it also removes heat from the area immediately around the sample before this heat can be transmitted to the rest of the calorimeter.

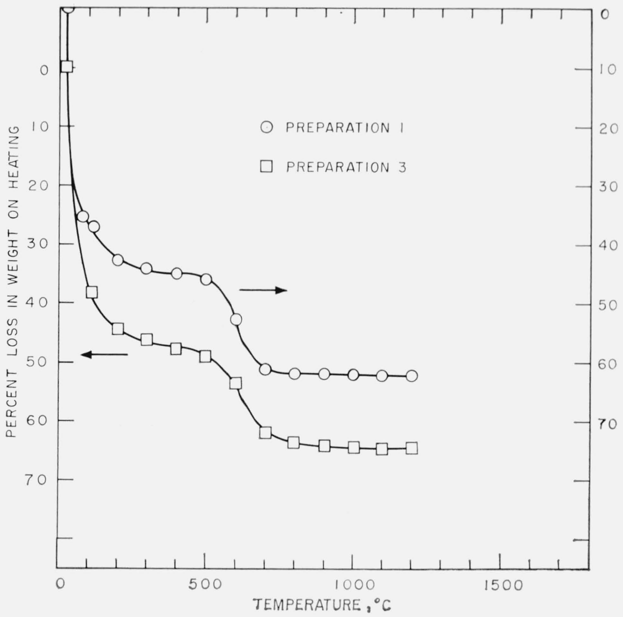

FIGURE 2. *Weight loss of preparations of calcium aluminate tricarbonate heated to constant weight at constant temperatures from 80 to 1200 °C.*

The problem was met in the case of $CaCO_3$ [7] by holding the sample under distilled H_2O in a glass bulb, breaking the bulb, and allowing the acid to rise through the sample as the sample fell into the acid. Rising bubbles gave up their sensible heat to the distilled H_2O. A heat-leakage constant obtained from calibration determinations was combined with an initial rating period (before breaking the bulb) to obtain the stirring energy effect for the particular run. It was then possible, for each 1 or 2-min period after breaking the bulb, to subtract the temperature rise due to heat leakage and to stirring energy from the observed temperature rise. This corrected temperature rise showed the rapid increase due to solution of the sample, followed by a gradual decrease due to CO_2 escape. By extrapolating the descending curve backwards to zero time (when the bulb had been broken), the temperature rise was obtained for solution of the entire sample with dissolved CO_2 as a product.

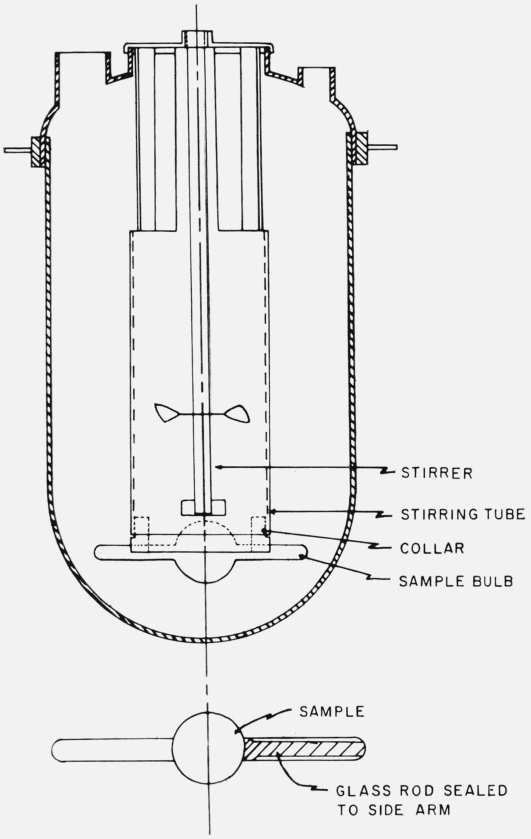

FIGURE 3. *Modifications in the calorimeter of reference* [7], *showing sealed glass sample bulb, plastic stirrer, and plastic collar on stirring tube.*

Enlarged view shows details of sample bulb.

This technique, used for $CaCO_3$, was not found necessary for calcium aluminate monocarbonate [7]. The tricarbonate samples, however, behaved more like $CaCO_3$, but the gradual decline in the corrected temperature rise was not as protracted. It was therefore possible in many determinations to obtain a final as well as an initial rating period, from which both the heat leakage and the stirring energy could be calculated.

Two methods of placing and breaking the bulb were used. For preparations 1 and 2, the "hanging-bulb" arrangement is shown in figure 1 of reference [7], where the bulb is drawn with dashed lines. The sample was released by dropping a 10-g weight onto the end of a glass rod, which in turn pierced the bottom of the bulb. Because of the uncertainty of defining how much of the mass of the bulb, rod, and connecting tubing was to be included within the calorimeter boundaries for the purpose of calculating heat capacity, an electrical calibration was first made, the entire assembly (calorimeter and jacket) cooled, and then the heat-of-solution determination performed, both determinations over approximately the same temperature range. A few determinations were made without calibrating; an average heat capacity was used, corrected for the differences in the masses of bulbs and samples within the calorimeter.

For preparations 3 and 4, and for the reported results of preparation 2, a sealed-bulb arrangement was used, as shown in figure 3. The bulb was centered between two side-arms, one closed at the bulb end to keep the sample from being trapped in that arm. A plastic collar was fitted to the bottom of the stirring tube, provided with grooves to hold the arms of the bulb. Some of the material was placed in the bulb through the open arm, the interior of the arm wiped clean, the sample weighed, and the open arm sealed at the tip. The bulb was centered on the bottom of the calorimeter and the stirring tube then inserted so that the grooves in the plastic ring were alined with the bulb arms. After assembly of calorimeter and jacket, acid was introduced gently to allow the bulb to float until the arms made contact with the plastic ring. To introduce the sample into the acid, the stirrer motor was stopped long enough to allow the stirrer to be pushed down against the bulb, a matter of 10 to 15 sec. A plastic stirrer replaced the normal platinum stirrer to provide the stiffness needed to break the bulb.

The sealed-bulb arrangement was adopted because the liquid placed over the sample in the hanging bulb is believed to have introduced errors in the thermochemical results. Water, used in preparation 1, although suitable for $CaCO_3$, may have further hydrated the samples and produced low heat-of-solution values. Dry *n*-propanol, completely miscible with water and possessing about the same vapor pressure at 25 °C, was used with preparation 2 to avoid the hydration effect, but it is probable that it dehydrated the samples to produce high heat-of-solution values.

Heats of solution for preparation 2 closer to those of preparations 3 and 4 were obtained when the sealed bulb was used in place of the hanging bulb. They were not considered reliable, however, because the preparation appeared to be slightly contaminated when the sealed-bulb determinations were made.

With the hanging bulb the acid charge was 740.00 g. It was not possible in the sealed-bulb technique to weigh the acid because of the conditions of assembly. The charge in this case was about 730 ml (755 g) and calibration was necessary for each determination. Calibration and heat of solution were not run over the same temperature range in preparations 3 and 4 because it was believed that cooling the jacket between the two runs upset the equilibrium of the initial rating period of the second (solution) run. The validity of calibrating at a lower temperature and dissolving the sample at a higher temperature was checked in one determination in which two calibrations were run, at both temperature levels. Several determinations were also made in which calibration and solution temperature levels were reversed.

Calorimeter samples were about 1 g for the samples dried at 79 percent relative humidity. The sample weights for material dried at lower humidities were smaller and contained the same molar quantity of calcium aluminate tricarbonate as the higher-humidity samples.

TABLE 3. *Properties of the preparations of calcium aluminate tricarbonate dried at relative humidities of 12 percent and less*

Desiccant	LiCl	$20N$ H_2SO_4	$23N$ H_2SO_4			CaO	
Relative humidity, percent	12	10	5			0	
Time exposed, days	17	[a] 9	[b] 1	[c] 20	[c] 28	49	49
Original preparation	4	4	4	3	3	3	4
Molar ratio, $H_2O:Al_2O_3$	27.51_7	25.89_5	24.32_2	15.16_1	12.56_8	5.89_4	5.84_0
Molar ratio of H_2O to $3CaO \cdot Al_2O_3 \cdot 3CaCO_3$, (n)	27.39_9	25.77_7	24.20_4	14.96_9	12.36_5	5.66_5	5.72_2
Heat of solution of sample, ΔH J/g	-435.9_8	-466.6_1	-473.6_9	-706.7_3	-781.2_6	-1000.2_0	-937.3_7
Corrected heat of solution of the $3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot nH_2O$ ΔH J/g	-494.8_3	-532.3_9	-542.5_7	-786.1_7	-878.2_1	-1158.9_5	-1162.6_0
kJ/mole	-526.5_4	-550.9_4	-546.1_0	-660.4_9	-696.6_2	-779.4_2	-783.0_7

[a] Exposed 17 days to LiCl before exposure to $20N$ H_2SO_4

[b] Exposed 10 days to $20N$ H_2SO_4 and 17 days to LiCl before exposure to $23N$ H_2SO_4

[c] Exposed 34 days to LiCl before exposure to $23N$ H_2SO_4

To conform to eq (1), the corresponding sample weights for reactants $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $CaCO_3$ are 0.34 and 0.27 g, respectively, when dissolved in 740–760 g of calorimeter acid. This compares with sample weights ranging from 0.26 to 0.44 g of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ actually used with 600 g of acid in earlier work [6, 7], which cover the desired sample-acid ratio. The heat of solution of 0.24 to 0.27 g of $CaCO_3$ in 740 g of acid was separately determined for this work because this sample-acid ratio had not been covered in reference [7].

The heat effect of adding the 24 moles of H_2O appearing in eqs (1) and (4) was estimated as the partial molal heat content of H_2O in 2N HCl [4], neglecting the contribution of the small amounts of other solutes present.

4. Results and Discussion

4.1. Heat of Solution of the Preparations

The heats of solution obtained with the original preparations (dried at 79 % relative humidity) are shown in table 1. Those obtained for the lower-humidity preparations are shown in table 3. Both tables also show heats of solution of the pure calcium aluminate tricarbonate, after correction for the impurities in the sample.

Detailed data of the heat-of-solution determinations for calcium carbonate, sucrose, and preparations 3 and 4, are shown in table 4.

4.2. Correction for Impurities

The calculation of the composition of a sample and of the heat of solution of the pure calcium aluminate tricarbonate present was performed as described in the appendices to references [6] and [7]. The nature of the impurities was suggested by the chemical analysis and its departures from the theoretical ratios for calcium aluminate tricarbonate. Inasmuch as departure from stoichiometry is often ascribed to analytical error, it is helpful to calculate what degree of uncertainty in the values obtained for impurities is attributable to the analysis; therefore, the precision of the impurity contents was calculated from the observed precision of the analyses. In general, the precision figures indicate that most of the values for the impurities are reliable to about 0.01 mole per mole of major component.

The nature of the sucrose impurity was not ascertained. X-ray patterns showed none of the lines of pure sucrose, and it was not possible to obtain a powder sample of calcium saccharate sufficiently free of H_2O to produce a crystalline diffraction pattern. The large variation of sucrose content from one preparation to another (between 6 and 12%) casts doubt on the hypothesis that the sucrose forms a part of the tricarbonate crystal structure. Microscopical examination showed some irregular crystals with positive elongation and refractive indices slightly greater and slightly less than 1.56, which may be attributed to sucrose, but they were less numerous than would be expected from the chemical analysis. DTA patterns and chemical analysis showed that the preparations contained organic matter that charred easily and was oxidized at about the same temperatures as pure sucrose. Consequently, for the purpose of correcting the observed heats of solution, the sucrose was treated as an impurity in its original form.

The following values were used for the heats of solution of the various impurities:

$CaCO_3$	$\Delta H = -354.00$ J/g (table 4)
$Ca(OH)_2$	-1763.95 J/g [14]
$Al_2O_3.3H_2O$	-210.62 kJ/mole [7]
sucrose	$+23.0$ J/g (table 4).

Of the three determinations made of the heat of solution of sucrose, the one involving the largest sample was used (table 4, sucrose, run 2) because the greater temperature change could be measured more precisely. Note, however, that the values of the other two determinations agree quite well with that of the determination chosen.

TABLE 4. *Heat-of-solution determinations*

Preparation	Run	Calibration								Solution				
		Initial temp.	Time	Voltage	Current	Heater resistance	Electrical energy	Corrected temp. rise	Heat capacity	Initial temp.	Sample weight	Corrected temperature rise	Heat of solution ΔH	Standard error
		Ohm	*sec*	*Volt*	*A*	*Ohm*	*Joules*	*Ohm*	*J/ohm*	*Ohm*	*g*	*Ohm*	*J/g*	*J/g*
3	1	2.5413	479.993	9.16192	0.132471	69.021	583.750	0.020089	29,058.2	2.5702	0.9993	0.014240	−414.07	
	2	2.5401	599.993	9.17883	.132974	69.027	732.319	.025135	29,135.4	2.5726	1.0030	.014205	−413.74	
	3	2.5426	599.993	9.23737	.133831	69.023	741.739	.025455	29,139.2	2.5750	1.0236	.014570	−414.77	
		Mean, before correction for impurities											−414.19	0.30
4	1	2.5404	599.993	9.142048	.132442	69.027	726.466	.025049	29,001.8	2.5726	1.0286	.014360	−404.89	
	2	2.5501	599.993	6.40689	.092746	69.080	356.524	.012233	29,144.4	2.5705	1.1663	.015935	−398.20	
	3	2.5402	599.993	9.17778	.132966	69.024	732.191	.025146	29,177.6	2.5721	1.0393	.014364	−402.34	
	4	2.5403	599.993	9.17746	.132952	69.029	732.086	.025184	29,069.5	2.5741	0.9907	.013646	−400.41	
	5	2.5400	599.993	9.15160	.132580	69.027	727.984	.025042	29,070.5	2.5723	1.0299	.014378	−405.83	
	6	2.5399	599.993	9.16357	.132763	69.022	729.942	.025162	29,009.7	2.5722	1.0414	.014519	−404.39	
		Mean, before correction for impurities											−402.68	1.2
4(12 R.H.)														
	1	2.5399	599.993	9.07363	.131471	69.016	715.743	.024554	29,149.8	2.5711	0.8972	.013452	−437.07	
	2	2.5479	599.993	9.06777	.131376	69.021	714.764	.024635	29,014.2	2.5789	1.0510	.015753	−434.88	
		Mean, before correction for impurities											−435.98	1.1
4(10 RH)		2.5409	599.993	8.24040	.119386	69.023	590.266	.020348	29,008.3	2.5674	0.9352	.015043	−466.61	
4(5 RH)		2.5657	599.993	8.19526	.118737	69.020	583.842	.020051	29,117.8	2.5402	0.9003	.014646	−473.69	
3(5 RH)		2.5696	599.993	8.67179	.125633	69.025	653.670	.022520	29,026.8	2.5399	0.7774	.018928	−706.73	
3(5 RH)		2.5701	599.993	8.20185	.118819	69.028	584.714	.020138	29,035.4	2.5407	0.7147	.019231	−781.26	
3(0 RH)		2.5463	599.993	8.71194	.126235	69.014	659.843	.022483	29,348.0	2.5754	0.6610	.022483	−1000.20	
4(0 RH)		2.5721	599.993	8.72583	.126420	69.023	661.864	.022761	29,078.5	2.5408	0.6501	.020956	−937.37	
[a] $CaCO_3$	[b] 1								[d] 28,845.8	----------	0.2492	.003930	[e]−354.37	
	[c] 2								[d] 28,770.2	----------	0.2710	.003977	[e]−353.62	
		Mean											−354.00	0.38
Sucrose	[a]1								[d] 28,590.1	----------	0.4511	−.00032	+20.3	
	2								[d] 29,054.1	2.6057	1.1700	−.000928	+23.0	
	3	2.6095	239.993	8.99702	.130282	69.058	281.308	.009653	29,142.0	2.6092	0.1103	−.000085	+22.5	

Calibrations on the same charge at different initial temperature levels.

Preparation	Run	Initial temp.	Time	Voltage	Current	Heater resistance	Electrical energy	Corrected temp. rise	Heat capacity	Initial temp.	Sample weight	Corrected temperature rise	Heat of solution ΔH	Standard error
	1	2.5398	599.993	9.18300	.133044	69.022	733.038	.025070	29,239.6					
	2	2.5828	419.993	9.18084	.133005	69.026	512.854	.017536	29,245.8					

[a] Hanging-bulb technique for $CaCO_3$ and sucrose, run 1. Sealed-bulb for all other determinations.
[b] Determined without the addition of tricalcium aluminate.
[c] Determined in acid to which 0.3268 g of tricalcium aluminate hexahydrate had been added.
[d] Heat capacity calculated from an average of previous runs and corrected for difference in weights of sample, bulb, and water in bulb.
[e] Total energy in each run corrected for energy of dilution of acid with water.
Run 1—7.6780 g H_2O, total energy 113.36 J, dilution energy 25.05 J, solution energy 88.31 J.
Run 2—5.6985 g H_2O, total energy 114.42 J, dilution energy 18.59 J, solution energy 95.83 J.

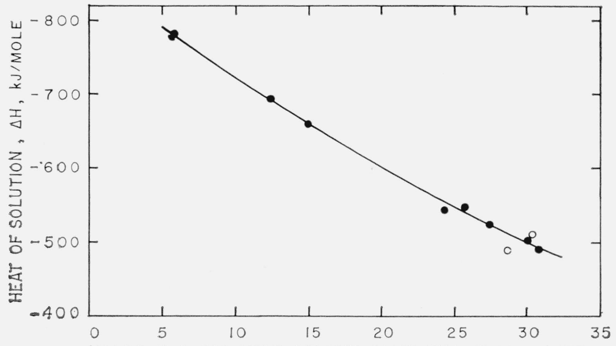

FIGURE 4. *Heat of solution of* $3CaO{\cdot}Al_2O_3{\cdot}3CaCO_3{\cdot}nH_2O$ (c).

Closed circles represent samples of preparations 3 and 4. Open circles represent samples of preparations 1 and 2. The solid curve was obtained from the closed circles.

The estimated standard error in the corrected heats of solution (calculated as described in the appendix) is about 2 kJ per mole. The poor precision of the sucrose analyses (which results from the poor precision of the determination of CO_2 by ignition) does not seriously affect the standard error of the corrected heats of solution because it enters only one of the minor terms in the calculation.

4.3. Heat of Solution of Calcium Aluminate Tricarbonate

Figure 4 is a plot of the corrected heats of solution against the calculated H_2O content of the pure compound. The points are derived from tables 1 and 3. The solid curve represents the following quadratic equation calculated by least squares from the points:

$$\Delta H = -865.566 + 15.2184n - 0.10296n^2 \qquad (6)$$

where

ΔH=heat of solution in kJ/mole calcium aluminate tricarbonate.
n=moles H_2O/mole calcium aluminate tricarbonate.

The curve was obtained only from the closed circles, representing preparations 3 and 4. Open circles refer to the corrected heats of solution of preparations 1 and 2, which were not used in calculating the equation, for reasons discussed in section 3.

The crystal structure of some of the complex calcium aluminates remains intact as the H_2O content is decreased [8] although the interplanar spacings may change. However, the x-ray patterns of the tricarbonate samples dried at relative humidities of 12 percent and less showed no change in interplanar spacings, but did show a progressive loss of intensity with complete disappearance of the peaks at $6H_2O$ and little evidence of them at $14H_2O$. The microscope revealed increasing quantities of trapezoidal plates with positive elongation and refractive indices of 1.523 and 1.545, suggestive of calcium aluminate monocarbonate or tetracalcium aluminate ($3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$), but quite different in appearance from the crystals of these compounds usually observed. Evidently there was decomposition or loss of crystallinity accompanying the loss of H_2O and there is some indication in the x-ray patterns that much of this change took place between 26 and $24H_2O$. It is possible that the lower H_2O contents represent mixtures of $30H_2O$ material and decomposition products.

From eq (6), the heat of solution of $3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 30H_2O$ in 2.00*N* HCl (at a sample-solution ratio of 1:755) is $\Delta H = -501.68$ kJ/mole. The change of heat of solution with H_2O content at this point, $d(\Delta H)/dn$, is 9.0_4 kJ/mole per mole H_2O.

4.4. Heat of Formation of the Product From the Reactants

The heat of the reaction represented by eq (1) is calculated from the heats of solution of the reactants and products. The heat effects of eqs (2), (3), (4), and (5) are added, as follows:

$$\begin{array}{lr}
\Delta H_2 = -580.36 \text{ kJ/mole} & \text{eq (2)} \\
\Delta H_3 = -106.29 & \text{eq (3)} \\
\Delta H_4 = -1.61 & \text{eq (4)} \\
-\Delta H_5 = +501.68 & -\text{eq (5)} \\
\hline
\Delta H_1 = -186.58 & \text{eq (1)}
\end{array}$$

The heat effect of eq (2) was obtained from the value of 1546.93 J/g for a sample of $3CaO \cdot Al_2O_3 \cdot 5.859H_2O$ [7], by correcting for its impurity content of 0.007 mole $CaCO_3$ per mole Al_2O_3 [6], and subtracting the correction of 0.46 kcal/mole (1.925 kJ/mole) discussed in reference [8].

4.5. Heat of Formation of Calcium Aluminate Tricarbonate From the Elements

The heat of formation of calcium aluminate tricarbonate is the sum of the heat effect of eq (1) and of the heats of formation of the reactants [3]:

$$\begin{array}{lr}
\Delta H^\circ_f,\ 3CaO \cdot Al_2O_3 \cdot 6H_2O \text{ (c)} & = -5561. \\
\Delta H^\circ_f,\ 3CaCO_3 \text{ (c)} & = -3620.624 \\
\Delta H^\circ_f,\ 24H_2O\text{(l)} & = -6860.16 \\
\Delta H, \text{ eq (1)} & = -186.58 \\
\hline
\Delta H^\circ_f,\ 3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 30H_2O \text{ (c)} & = -16{,}228._{36} \\
 & \text{kJ/mole.}
\end{array}$$

4.6. Summary of Heats of Formation and Heats of Reaction

The results of this paper and of references [6, 7, 8] may be combined and updated to produce the following thermochemical data on complex calcium aluminates:

Heats of Formation, ΔH°_f

$3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 30H_2O$ (c)	$-16{,}228._{36}$ kJ/mole
$3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10.68H_2O$ (c)	$-8{,}188._{76}$
$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ (c)	$-17{,}548._{38}$
$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ (c)	$-17{,}252._{06}$
$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ (c)	$-8{,}788._{19}$

Stepwise Heats of Reaction, ΔH

$$3CaO \cdot Al_2O_3 \cdot 6H_2O \text{ (c)} + CaCO_3 \text{ (c)} + 4.68H_2O \text{ (l)} \rightarrow 3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10.68H_2O \text{ (c)} \qquad \Delta H = -83.16 \text{ kJ}$$

$$3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10.68H_2O \text{ (c)} + 2CaCO_3 \text{ (c)} + 19.32H_2O \text{ (l)} \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 30H_2O \text{ (c)} \qquad \Delta H = -103.42 \text{ kJ}$$

$$3CaO \cdot Al_2O_3 \cdot 6H_2O \text{ (c)} + CaSO_4 \cdot 2H_2O \text{ (c)} + 4H_2O \text{ (l)} \rightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O \text{ (c)} \qquad \Delta H = -62.71 \text{ kJ}$$

$$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O \text{ (c)} + 2(CaSO_4 \cdot 2H_2O) + 15H_2O \text{ (l)} \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O \text{ (c)} \qquad \Delta H = -134.02 \text{ kJ}$$

$$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O \text{ (c)} + 2(CaSO_4 \cdot 2H_2O) \text{ (c)} + 16H_2O \text{ (l)} \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \text{ (c)} \qquad \Delta H = -144.50 \text{ kJ}$$

5. Appendix

The standard errors of the mole ratios and the standard errors of the corrected heats of solution, arising from the estimated standard errors of the original analytical determinations and heat-of-solution determinations, were calculated directly from the original independently measured quantities by the general formula for propagation of error for independent variables

$$S_F=\sqrt{\left[\frac{\partial F}{\partial_x}\right]^2 S_x^2+\left[\frac{\partial F}{\partial_y}\right]^2 S_y^2+\left[\frac{\partial F}{\partial_z}\right]^2 S_z^2+\ .\ .\ .}$$

where S_F is the standard error of the function $F(x, y, z, \ .\ .\ .\ )$ and $S_x, S_y, S_z, \ .\ .\ .$ are the standard errors of $x, y, z, \ldots$, respectively, and the partial derivatives are to be evaluated at the averages of the variables [15]. The independently measured quantities were: CaO, Al_2O_3, loss on ignition, CO_2 by acid attack, CO_2 by ignition, heat of solution of the preparation, and heat of solution of $CaCO_3$. Also treated as an independent quantity was the heat of solution of $Ca(OH)_2$, obtained from triplicate determinations in [14]. By making each standard error calculation directly from the original independent quantities, the effects of cross-correlation obtained in stepwise calculation were eliminated.

6. References

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