TABLE III

EFFICIENCY OF QUENCHING COLLISIONS

Quenching gas	a, mm.$^{-1}$	$p_{1/2}$, mm.	$\sigma_{12}^2\tau \times 10^{21}$ cm.^{2} sec.	Relative efficiency	$\sigma_{12} \times 10^8$ ($\tau = 10^{-7}$ sec.), cm.
NO_2	50	0.020	9.3	1	31
CO_2	44	.023	8.2	0.87	29
N_2	21	.048	2.7	.29	16
O_2	16.5	.061	2.2	.24	15
H_2	26	.038	1.4	.15	12

Summary

The intensity of fluorescence excited in nitrogen dioxide by the 4358 and 4047 Å. lines of the mercury arc has been determined for the pressure range 0.001 to 18 mm. Nitrogen dioxide is very efficient as a quenching agent; the fluorescence is half damped at a pressure of 0.02 mm. The product of the square of the effective diameter for collision and the life of the excited molecule $\sigma_{12}^2\tau$ is 9.3×10^{-21} cm.^{2} sec. This result indicates a deactivational diameter approximately ten times greater than kinetic theory values.

It is shown that the quenching of this fluorescence by foreign gases is in quantitative agreement with Equation 7, which is based on the occurrence of deactivating collisions with these gases as well as with nitrogen dioxide itself. There is specificity in quenching by added gases; the relative deactivational efficiencies of carbon dioxide, nitrogen, oxygen and hydrogen referred to nitrogen dioxide as unity are, respectively, 0.87, 0.29, 0.24 and 0.15.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SASKATCHEWAN, SASKATOON, SASKATCHEWAN]

STUDIES ON THE THERMOCHEMISTRY OF THE COMPOUNDS OCCURRING IN THE SYSTEM $CaO-Al_2O_3-SiO_2$. IV. THE HEAT OF SOLUTION OF TRICALCIUM ALUMINATE AND ITS HYDRATES IN HYDROCHLORIC ACID[1]

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The heats of solution of the compounds occurring in the system $CaO-Al_2O_3-SiO_2$ and of their hydration products are of interest not only for the purpose of calculating the heat of formation of these compounds but also in connection with problems relating to the constitution of hydraulic cements and elucidation of the reactions which take place during their hydration. This applies especially to the aluminates and the silicates of calcium which are rich in lime. The paucity of such data is probably mainly due to the difficulty of preparing sufficient quantities of these substances in a pure

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[1] The authors wish to acknowledge generous financial assistance from the National Research Council of Canada.

state. The present paper describes the determination of the heats of solution of tricalcium aluminate and its hydrates in $HCl \cdot 20H_2O$ and $HCl \cdot 200H_2O$.

Apparatus and Experimental Procedure.—The calorimeter, which was of the Richards adiabatic type with a slight modification, the Beckmann thermometers used, the method of introducing the sample into the calorimeter and the limits of adiabatic control have been described elsewhere.[2]

The general procedure used was to determine the heat of solution of the aluminate in $HCl \cdot 20H_2O$. The heat of dilution of $HCl \cdot 20H_2O$ and of the resulting solution of aluminate, when diluted to a concentration corresponding to $HCl \cdot 200H_2O$, was determined by the method of Richards, Rowe and Burgess,[3] and the heat of solution of the aluminate in $HCl \cdot 200H_2O$ then calculated according to the usual method.[3]

Preparation of Materials

Calcium Carbonate and Alumina.—The method of purification of the calcium carbonate was similar to that already described.[2a] The aluminum hydroxide was purified by precipitation from a boiling 2% solution of ammonia alum which was free from iron, using redistilled ammonia water; the precipitate was washed thoroughly by decantation, filtered off, washed, redissolved in pure hydrochloric acid, the solution diluted to the original volume and the precipitation as aluminum hydroxide repeated. After thorough washing, the aluminum hydroxide was dried in a covered platinum dish and ground to pass a 200-mesh sieve. The material had an ignition loss of about 30%.

Tricalcium Aluminate. Sample 1.—Calcium carbonate and aluminum hydroxide, prepared as described above, were mixed wet in the proportions $3CaO:Al_2O_3$. The water was then evaporated with constant stirring of the mixture to prevent segregation. When dry, the material was transferred to platinum crucibles, placed in a platinum-wound resistance furnace, the temperature gradually raised to 1300° and kept there for several hours. The sintered mass was then broken up, ground in an agate mortar to pass a 200-mesh sieve, and the heating repeated, the temperature being raised to about 1370°. Microscopic examination showed that even after several heat treatments at 1370° the material contained small amounts of free lime and $5CaO \cdot 3Al_2O_3$. It was found that treating the finely powdered material with water aided combination materially during the subsequent heat treatment. due probably to dispersion of the free lime by hydration. The treatment, however, seemed to cause tiny voids to be formed in the crystals of tricalcium aluminate and this made exact microscopic examination more difficult. These voids were eliminated by subsequent heat treatments. The material was repeatedly ground and reheated until White's test[4] indicated absence of free lime, and careful examination by the petrographical microscope showed that the sample was homogeneous and free from particles of lime and $5CaO \cdot 3Al_2O_3$. It was composed of isotropic crystals, with a refractive index of 1.710 ± 0.002.

Sample 3.—Sample 3 was prepared in the same way as Sample 1. This sample, however, contained a small amount of $5CaO \cdot 3Al_2O_3$ but no free lime. Table I gives the analysis of the two samples.

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[2] (a) Thorvaldson, Brown and Peaker, THIS JOURNAL, **51**, 2678 (1929); (b) Thorvaldson and Brown, *ibid.*, **52**, 80 (1930).

[3] Richards. Rowe and Burgess, *ibid.*, **32**, 1176 (1910).

[4] White, *J. Ind. Eng. Chem.*, **1**, 5 (1909).

TABLE I

ANALYSES OF TRICALCIUM ALUMINATE[a]

	Sample 1	Sample 3	Calcd.
Calcium oxide (CaO)	62.31	61.98	62.27
Alumina (Al_2O_3)	37.76	37.98	37.73

Ferric oxide, alumina and silica were absent from both samples.

[a] Analyses by David Wolochow.

$HCl\cdot20H_2O$.—C. P. acid was redistilled through a partly refluxing quartz condenser, the middle portion of the distillate collected in silica flasks and adjusted to $HCl\cdot20H_2O$, the concentration being determined both by titration with pure sodium carbonate and by gravimetric determination of chloride.

The Specific Heat of $HCl\cdot20H_2O$

Recent determinations of the specific heat of hydrochloric acid of various concentrations by Richards, Mair and Hall[5] have given values which differ somewhat from the previously accepted ones. Unfortunately the specific heat of $HCl\cdot20H_2O$ was not included among those redetermined. It was therefore decided to determine the specific heat of $HCl\cdot20H_2O$ over both the temperature intervals 16 to 20 and 18 to 20°. The acid used in this determination was purified with special care and gave the composition $HCl\cdot20.01H_2O$ by titration with sodium carbonate and $HCl\cdot20.02H_2O$ by gravimetric analyses of chloride.

The method used for the determination of specific heat was that of Richards and Rowe.[6] The calorimeter can was of pure gold, while containers for the sulfuric acid and alkali were made of a gold alloy (80% gold and 20% copper). This alloy was not attacked appreciably during the series of experiments by the solutions in contact with it.

The concentrations of sulfuric acid and sodium hydroxide used for the series for the interval 16 to 20° were: H_2SO_4, 6.928%; NaOH, 27.73%; and for the series for the interval 18 to 20°: H_2SO_4, 4.235%; NaOH, 13.86%. As practically the same weights of the acid and alkali were used for each determination and as both the water standardization and the determinations of specific heat covered exactly the same temperature range it was not necessary to know the specific heats of these solutions with a high degree of accuracy. The following values for specific heats were used: H_2SO_4 (6.928%), 0.94; H_2SO_4 (4.235%), 0.96; NaOH (27.73%), 0.83; NaOH (13.86%), 0.87.

Tables II and III give the experimental data for the determinations over the interval 16 to 20°. In Table II, Q_{100} represents the heat evolved during the neutralization of 100.0 g. of the solution of sulfuric acid, at 20°.

A similar series of experiments, including water standardization, was made with the same solution of hydrochloric acid over the temperature

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[5] Richards, Mair and Hall, THIS JOURNAL, **51**, 727 (1929).

[6] Richards and Rowe, *Proc. Am. Acad. Arts Sci.*, 49, 175 (1913).

TABLE II

WATER STANDARDIZATION

Total heat capacity, 510.3 cal./deg. Weight of water, 400.5 g. Weight of NaOH solution, 17.09 g.

Expt.	H_2SO_4 soln., g.	Final temp., °C.	Corr. rise,[a] °C.	Q_{100}, calories
1	85.116	20.01	3.989	2391.6
2	85.098	19.99	3.982	2387.9
3	85.102	19.99	3.985	2389.6
4	85.102	19.99	3.986	2390.2
5	85.102	19.99	3.985	2389.6
Mean		19.99	3.985	2389.2

TABLE III

SPECIFIC HEAT OF $HCl \cdot 20H_2O$

Heat capacity of apparatus, H_2SO_4 and NaOH, 109.8 cal./deg. Weight of $HCl\cdot 20H_2O$, 470.6 g. Weight of NaOH solution, 17.09 g.

Expt.	H_2SO_4 soln., g.	Final temp., °C.	Corr. rise,[a] °C.	Specific heat[b] $HCl\cdot 20H_2O$ Mean cal. 16–20°
1	85.105	19.99	3.987	0.8505
2	85.096	20.09	3.985	.8508
3	85.115	19.96	3.988	.8507
4	85.103	20.01	3.987	.8507
5	85.120	19.99	3.986	.8512
6	85.119	19.97	3.989	.8505
Mean		20.00	3.987	.8507

[a] The temperature rise is corrected for exposed stem, setting and stirring. [b] As the average final temperature of the water standardization series was 19.99° and the temperature coefficient for the neutralization of sulfuric acid is fairly large, a small correction was applied in Expts. 2, 3, 4 and 6 of Table III for the variation in the final temperature from 19.99°. For this purpose the temperature coefficient given by Richards and Rowe[7] (−49.5 cal. per $^1/_2$ mole H_2SO_4 per °C.) and the average value for the heat of neutralization of 100 g. of 6.928% H_2SO_4 obtained in Table II were used.

interval 18–20°. The value obtained for the specific heat of $HCl\cdot 20H_2O$ over this range was 0.8510 (mean calorie 18–20°).

The value 0.8507 for the specific heat of $HCl\cdot 20H_2O$ over the range 16–20° is considerably higher than the preliminary value of 0.8487 given by Richards and Rowe.[7] It may, however, be shown that our result is consistent with those of Richards, Mair and Hall[5] for more dilute solutions of hydrochloric acid by plotting the apparent molal heat capacity with the square root of the molality as Randall and Rossini[8] have done for a number of electrolytes. This provides an extremely sensitive graphical method of comparing the results (Fig. 1).

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[7] Richards and Rowe, THIS JOURNAL, **42**, 1621 (1920).

[8] Randall and Rossini, *ibid.*, **51**, 323 (1929); Rossini, *Bur. Stands. J. Res.*, **4**, 313 (1930).

The Heat of Solution of Tricalcium Aluminate in $HCl \cdot 20H_2O$ and in $HCl \cdot 200H_2O$

The results of the determinations of the heat of solution of tricalcium aluminate, Sample No. 1, in $HCl \cdot 20H_2O$ are given in Table IV. The specific heats used in calculating the heat capacity of the calorimeter system were: gold, 0.031; gold alloy (80% Au, 20% Cu), 0.44; $HCl \cdot 20H_2O$ (16–20°), 0.8507, (18–20°), 0.8510. The specific heat for $HCl \cdot 20H_2O$ is in terms of the specific heat of water over the same temperature interval. All weights were corrected to vacuum.

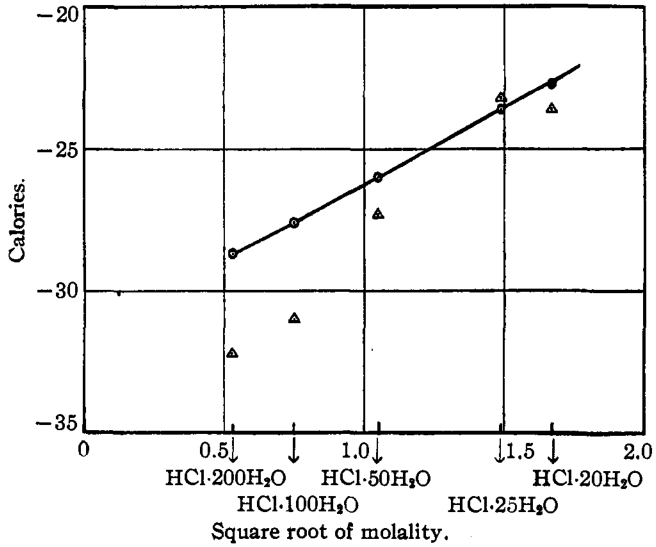

Fig. 1.—Apparent molal heat capacity of HCl at 18°. ⊙, Richards, Mair, and Hall; △, Richards and Rowe; ●, Thorvaldson, Brown and Peaker ($HCl \cdot 20H_2O$).

From Table IV one finds that the average proportion of aluminate to acid is 1 g. to 210.7 g. of $HCl \cdot 20H_2O$. In order to calculate the heat of solution of tricalcium aluminate in $HCl \cdot 200H_2O$ it is necessary to determine the heats of dilution of 210.7 g. of $HCl \cdot 20H_2O$ to $HCl \cdot 200H_2O$ and of 211.7 g. of the aluminate solution to a corresponding dilution. It is also necessary to determine the heat effect of mixing the resulting diluted solutions.

Ten determinations of the heat of dilution of $HCl \cdot 20H_2O$ to $HCl \cdot 200H_2O$ were made. The weight of $HCl \cdot 20H_2O$ used for each experiment was 61.21 g., the total heat capacity was 564 cal. and the final temperature 20.0°. The corrected rise varied from 0.150 to 0.152° with a mean of 0.1509°. The heat of dilution is therefore 85.11 calories for 61.21 g. or 293.0 calories for 210.7 g. of $HCl \cdot 20H_2O$.

In a similar way it was found that 211.7 g. of the aluminate solution gave

TABLE IV

HEAT OF SOLUTION OF $3CaO \cdot Al_2O_3$. SAMPLE 1, IN $HCl \cdot 20H_2O$

Weight of $HCl \cdot 20H_2O$, 600.4 g.

Expt.	$3CaO \cdot Al_2O_3$, g.	Final temp., °C.	Corr. rise,[a] °C.	Heat capacity,[c] 18° cal.	Heat of soln. per gram at 20°, $cal._{20°}$
1	2.8481	20.01	3.968	528.6	736.8
2	2.8649	19.95	3.991	528.6	736.7
3	2.8766	19.96	4.007	528.6	736.6
4	2.8034	19.99	3.971	519.0	735.5
5	2.8558	20.05	4.041	519.0	734.7
Mean		19.99			736.1
Corrected for evaporation[b]					736.4

[a] Corrected for stem exposed, setting of thermometer and stirring. [b] The volume of air in the calorimeter was about 600 cc. This was no doubt saturated with water vapor at the beginning of each run and probably nearly saturated at the end of each run. Three-fourths of the calculated correction for the heat of vaporization is applied. [c] The temperature of the sample of tricalcium aluminate when introduced into the calorimeter was 20°. The heat capacity of the aluminate is therefore not included in the calculated value.

on corresponding dilution the mean value of 289.4 calories. For this determination it was necessary to know the specific heat of the aluminate solution. Determinations made as for $HCl \cdot 20H_2O$ described above, gave 0.847 calorie per degree and this value was not found to vary appreciably for the different aluminate solutions used.

Experiments showed that there was no heat effect produced when $HCl \cdot 200H_2O$ was added to the diluted aluminate solution. Thus the heat of solution of $3CaO \cdot Al_2O_3$ in $HCl \cdot 200H_2O$ is independent of the proportion of aluminate to acid at least for proportions approximating those used. The calculated value for the heat of solution of $3CaO \cdot Al_2O_3$ in $HCl \cdot 200H_2O$ at 20° is therefore 732.8 (736.4 + 289.4 − 293.0) calories (20°) per gram.

The Heat of Solution of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ in Hydrochloric Acid.[9]—Thorvaldson and Grace[10] have shown that tricalcium aluminate forms a very stable hydrate of the composition $3CaO \cdot Al_2O_3 \cdot 6H_2O$. This hydrate is readily formed when tricalcium aluminate is hydrated in steam under pressure.

Determinations of the heat of solution of two samples of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ prepared from $3CaO \cdot Al_2O_3$, Sample 1, were made. Sample A was prepared by exposing the freshly ignited aluminate to saturated steam at 150° in an autoclave and drying the resulting hydrate to constant weight over calcium oxide. It was found that the $3CaO \cdot Al_2O_3$ had taken up 39.97% of water, which corresponds to a formula of $3CaO \cdot Al_2O_3 \cdot 5.99H_2O$.

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[9] The authors are indebted to Mr. Norman S. Grace for preparing the samples of the hydration products of tricalcium aluminate used in the determinations of the heat of solution.

[10] Thorvaldson and Grace, *Canadian J. Res.*, 1, 36 (1929).

Sample B was prepared by adding water to the anhydrous aluminate and drying to constant weight over calcium oxide, this process of treating with water and drying being repeated several times. The total increase in weight after drying over lime was 40.08%, which corresponds to a formula of $3CaO \cdot Al_2O_3 \cdot 6.01H_2O$.

Special precautions were taken to prevent access of the carbon dioxide of the air to the samples during the preparation of the hydrate. This could be effectively prevented in the case of the hydrate prepared in steam by taking care that the air and water in all vessels were free from carbon dioxide. There was a somewhat greater chance in the case of the sample prepared at room temperature for contact with ordinary air and there may have been a slight absorption of carbon dioxide. This probably accounts for the slightly lower heat of solution obtained for Sample B. Both samples were entirely isotropic and had an index of refraction,[11] N_{Na} 1.604 ± 0.002.

Table V

Heat of Solution of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ in $HCl \cdot 20H_2O$

Total heat capacity, 519.2 cal./deg. Weight of $HCl \cdot 20H_2O$, 600.4 g.

Sample	$3CaO \cdot Al_2O_3 \cdot 6H_2O$, g.[c]	$3CaO \cdot Al_2O_3$, g.	Final temp., °C.	Corr. rise,[a] °C.	Heat of soln.[b] at 20° cal.$_{20}$ per gram $3CaO \cdot Al_2O_3$
A		2.0961	20.06	2.114	523.8
A		2.1417	20.09	2.145	520.2
A		2.0596	19.85	2.083	525.3
A		2.0147	19.83	2.029	523.1
Average for Sample A			19.96		523.1
B	2.8448	2.0308	20.01	2.032	519.7
B	2.8502	2.0347	19.98	2.039	520.5
Average for Sample B			19.995		520.1
Average for Samples A and B					522.1

[a] Corrected for stem exposed, setting of thermometer and stirring. [b] Corrected for evaporation and from the 19° to the 20° calorie. [c] The temperature of the sample of hydrated tricalcium aluminate when introduced into the calorimeter was 20°. The heat capacity of the aluminate is therefore not included in the calculated value for heat capacity.

The heat of dilution of the aluminate solution obtained from the experiments recorded in Table V to a dilution corresponding to $HCl \cdot 200H_2O$ at 20° was determined. Four determinations gave exactly the same value, namely, 84.09 calories for the heat of dilution of 61.43 g. of the solution (that is, a temperature rise of 0.149° for a heat capacity of 564.4 cal./deg.). Considering the determinations with Sample A in Table V, the average weight of $HCl \cdot 20H_2O$ used per gram of anhydrous tricalcium aluminate was 288.9 g. and the corresponding average weight of aluminate solution pro-

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[11] Measurements by V. A. Vigfusson.

duced was 290.3 g. The heats of dilution amount to 401.7 and 397.4 calories, respectively.

The value for the heat of solution of $3CaO\cdot Al_2O_3\cdot 6H_2O$ (Sample A) in $HCl\cdot 200H_2O$ at 20° is therefore 518.8 $calories_{20°}$ per gram of anhydrous tricalcium aluminate or 370.6 $calories_{20°}$ per gram of the hydrate.

The calculated heat of hydration of tricalcium aluminate to the hexahydrate at 20° is 214.0 $calories_{20°}$ per gram or 57.8 kg. $calories_{20°}$ per formula weight.

Heats of Solution of Higher Hydrates of $3CaO\cdot Al_2O_3$

A crystalline hydrate of tricalcium aluminate occurring as hexagonal plates, needles and spherulites is well known. Attempts to obtain this hydrate in the pure state and determine its water of hydration have produced results which are apparently very discordant, Gallo,[12] Klein and Phillips[13] and Pulfrich and Linck[14] reporting a water content varying from 5.5 to 10.5 molecules. Later experimental work[15] has shown that special precautions must be taken in order to obtain this hydrate free from admixture of the isotropic hydrate $3CaO\cdot Al_2O_3\cdot 6H_2O$. Further, it appears that on drying, the crystalline hexagonal plates, which when formed in equilibrium with water near its freezing point probably have the composition $3CaO\cdot Al_2O_3\cdot 12H_2O$, give up their water of hydration in several steps without a material change in the crystalline form until exposure over calcium oxide produces a material of the composition $3CaO\cdot Al_2O_3\cdot 8H_2O$.

There seems, however, to be some doubt as to the existence of several anisotropic hydrates of tricalcium aluminate. It was thought that determinations of the heat of solution of hydrated material containing varying amounts of water might give an indication as to the way in which the water is held. In determining the heat of solution of calcium hydroxide in $HCl\cdot 200H_2O$ it was found[2b] that this substance is capable of taking up large quantities of water with only a very slight decrease in the heat of solution. As it is generally accepted that calcium hydroxide does not form a higher hydrate, a similar change in the heat of solution of hydrated tricalcium aluminate with increasing water content would suggest that the water is not bound chemically.

The higher hydrates of tricalcium aluminate were formed by the gradual addition of anhydrous tricalcium aluminate to carbon dioxide-free water, the mixture being cooled by ice. The hydrate was then kept in contact with water below 21° for about two weeks, after which portions were dried at 21° over saturated solutions of various salts. The method is described in detail elsewhere.[15]

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[12] Gallo, *Gazz. chim. ital.*, **38**, II, 156 (1908).

[13] Klein and Phillips, Techn. Paper No. 43, U. S. Bureau of Standards, **1914**.

[14] Pulfrich and Linck, *Kolloid-Z.*, **34**, 117 (1924).

[15] Thorvaldson, Grace and Vigfusson, *Canadian J. Res.*, **1**, 201 (1929).

The hydrates used for this series of determinations were prepared from $3CaO \cdot Al_2O_3$, Sample 3. This sample is slightly low in lime and contains therefore a small quantity of the aluminate next lower in lime, namely, $5CaO \cdot 3Al_2O_3$. On hydration this substance forms hydrated tricalcium aluminate with liberation of the excess of alumina as hydrate. It was found that the heat of solution of Sample 3 in $HCl \cdot 200H_2O$ was 9.3 calories per gram lower than that obtained with the purer Sample No. 1, but the heat of solution of the hydrate ($3CaO \cdot Al_2O_3 \cdot 6H_2O$) obtained by exposing Sample No. 3 to steam under pressure was also 9.4 calories lower than that for the corresponding product from Sample 1, giving a calculated heat of hydration of 214.1 for Sample 3 against 214.0 calories for Sample 1. There was therefore good reason to expect that the *differences* in the heat of solution of the various hydrates prepared from Sample 3 would not differ materially from those which would have been obtained with hydrates from the purer Sample, No. 1. Table VI gives the calculated heats of hydration of tricalcium aluminate to hydrates containing four different amounts of water.

TABLE VI

HEAT OF HYDRATION OF TRICALCIUM ALUMINATE CALCULATED FROM VALUES FOR HEATS OF SOLUTION OF THE HYDRATES IN $HCl \cdot 200H_2O$

Hydration of $3CaO \cdot Al_2O_3$	Heat effect, calories per gram of anhydrous aluminate
$3CaO \cdot Al_2O_3 \cdot 6.00H_2O$	214
$3CaO \cdot Al_2O_3 \cdot 8.00H_2O$	235
$3CaO \cdot Al_2O_3 \cdot 10.2H_2O$	251
$3CaO \cdot Al_2O_3 \cdot 11.6H_2O$	261

The values given in Table VI can be considered only as preliminary. The changes in the heat effect are rather larger than one would expect were the water adsorbed by $3CaO \cdot Al_2O_3 \cdot 8H_2O$, but are approximately proportional to the increase in H_2O in the material. The results can hardly be considered to give conclusive evidence as to the existence of several anisotropic hydrates of tricalcium aluminate.

The Heat of Formation of Tricalcium Aluminate.—The heat of formation of tricalcium aluminate from calcium oxide and aluminum oxide may be calculated from the heats of solution of these substances in hydrochloric acid. As no experimental value for the heat of solution of aluminum oxide in hydrochloric acid is available, this must also be calculated from other thermochemical data. Using the value 68.4 kg. cal. per mole for the heat of formation of water,[16] 127 kg. cal per gram atom as the heat of solution of aluminum in $HCl \cdot 200H_2O$,[3] and 190.0 kg. cal. per gram atom as the heat of combustion of aluminum,[17] we obtain 79.2 kg. cal. per mole for the heat of

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[16] Lewis, THIS JOURNAL, **28**, 1390 (1906).

[17] Roth and Müller, *Z. phys. Chem.*, **144**, 257 (1929).

solution of Al_2O_3 in $HCl{\cdot}200H_2O$. Combining this value with 46.5 kg. cal. per mole as the heat of solution of calcium oxide[2a] and 198 kg. cal. per mole as the heat of solution of tricalcium aluminate in $HCl{\cdot}200H_2O$, one obtains 20.7 kg. cal. per mole for the heat of formation of $3CaO{\cdot}Al_2O_3$ from CaO and Al_2O_3 at 20°.

Summary

1. The heat of solution of tricalcium aluminate in hydrochloric acid (1 g. of $3CaO{\cdot}Al_2O_3$ to 19.4 g. of HCl) was found to be 736.4 $cal._{20}$ per gram of $3CaO{\cdot}Al_2O_3$ in $HCl{\cdot}20H_2O$ or 732.8 $cal._{20}$ per gram in $HCl{\cdot}200H_2O$ at 20°.

2. The heat of solution of the isotropic (regular) hydrate of tricalcium aluminate ($3CaO{\cdot}Al_2O{\cdot}6H_2O$) in hydrochloric acid (1 g. of anhydrous $3CaO{\cdot}Al_2O_3$ to 26.5 g. of HCl) was found to be 523.1 $cal._{20}$ per gram of anhydrous aluminate in $HCl.20H_2O$ or 518.8 $cal._{20}$ per gram in $HCl{\cdot}200H_2O$ at 20°.

3. The heat of solution of tricalcium aluminate in $HCl{\cdot}200H_2O$ was found to be independent of the amount of acid of this concentration used in excess of the above ratio of aluminate to acid.

4. The calculated heat of hydration of tricalcium aluminate to the hexahydrate is 214 $cal._{20}$ per gram at 20°.

5. Preliminary values were obtained for the heat of solution in $HCl{\cdot}20H_2O$ of samples of anisotropic (hexagonal) hydrates of tricalcium aluminate containing 8, 10.2 and 11.6 moles of water of hydration per formula weight of $3CaO{\cdot}Al_2O_3$.

6. The specific heat of hydrochloric acid of the concentration $HCl{\cdot}20H_2O$ was determined between 16 and 20° as compared with water over the same temperature interval and the value 0.8507 was obtained.

7. The value of 77 calories per gram was obtained for the calculated heat of formation of tricalcium aluminate from lime (CaO) and alumina (Al_2O_3) at 20°.

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