

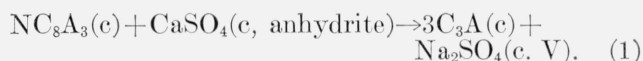
Heat of Formation of Sodium Calcium Aluminate

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The compounds $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, Na_2SO_4 V (Thenardite), $\text{Na}_2\text{O}\cdot 8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, and CaSO_4 , anhydrite, were prepared, and their heats of solution in HCl , $26.61\text{H}_2\text{O}$ were determined. The heat of solution of Na_2SO_4 V in water to form Na_2SO_4 , $1000\text{H}_2\text{O}$ was also measured. From these and other data in the literature the heats of formation of $\text{Na}_2\text{O}\cdot 8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ and NaSO_4 V were calculated to be -2576 and -330.92 kcal/mole, respectively.

1. Introduction

Investigations of the alkali phases in portland cement clinker, summarized by Newkirk [1],¹ have shown that the compound $\text{Na}_2\text{O}\cdot 8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, hereafter abbreviated NC_8A_3 ,² is formed. As part of a continuing investigation of the thermochemical properties of compounds occurring in hydraulic cements and their hydration products, the heat of formation of this compound was determined. No prior thermochemical data on NC_8A_3 have been found. Measurements were made at 25°C of ΔH of the reaction



This reaction occurs spontaneously [4] at high temperatures, where, however, the high-temperature form of calcium sulfate is present and liquid sodium sulfate is formed. The value of ΔH_1 was obtained by measuring the heats of solution of the four substances in hydrochloric acid solution. The heat of formation of NC_8A_2 was calculated from this value of ΔH_1 and the heats of formation of the other three substances taken from the literature.

2. Materials, Apparatus, and Procedure

Tricalcium aluminate was prepared by the method used by Thorvaldson, Brown, and Peaker [2]. The ignition loss of this material after grinding was 0.08 percent, assumed to be water in the compound C_3AH_6 formed by reaction of the anhydrous aluminate with the moisture in the air. Thenardite, Na_2SO_4 V [3], was crystallized from a 50-percent solution of Na_2SO_4 at 50°C by the slow addition of hot alcohol. The mixture was left on the steam bath for 2 hr and then filtered. The crystals were dried overnight at 100°C and ground to pass a No. 100 sieve. They were essentially free from inclusions, as judged by microscopical examination, and the loss in weight on heating for $2\frac{1}{2}$ hr at 950°C was 0.02 percent. In the measurements and calculations, this material was considered to be pure Na_2SO_4 . The compound NC_8A_3 was prepared as described by Newkirk [4], except that after heating once at $1,200^\circ\text{C}$ the preparation was autoclaved for several hours at 300 psi before repeated heating at $1,300^\circ\text{C}$ with intervening grinding and sieving. Microscopical examination and chemical analysis indicated that

the product was homogenous and of the proper composition. Anhydrite was prepared by first precipitating gypsum from a hot solution of CaSO_4 prepared from the hemihydrate and then converting the gypsum to anhydrite by heating for 2 hr at $1,000^\circ\text{C}$ [5].

Details of the calorimetric apparatus and procedure have been given elsewhere [6]. The calorimeter used in this work was a 1-pt wide-mouthed vacuum flask cemented to a metal flange. A brass cover with tubes for stirrer, thermometer, heater, and introduction of the sample was bolted to this flange, and the calorimeter was submerged 4 in. below the surface of a water bath controlled at 25.0°C . The cover was made watertight by means of an O-ring seal. The temperature of the bath remained constant to better than $\pm 0.002^\circ\text{C}$ during a determination. The calorimeter charge was 425.0 g of HCl , $26.61\text{H}_2\text{O}$ (2.000 normal at 25°C). The starting conditions were so adjusted that the final temperature of the calorimeter was as close as possible to 25.0°C . This procedure was adopted both to avoid the need for correcting the measured heat of solution to the standard temperature of 25°C and to prevent the distillation of water from a warmer surface of the acid solution to condense on a cooler inner surface of the metal cover. Because there was no other free water surface within the flask, condensation in the reverse direction was unlikely.

The weights of the samples for the heat-of-solution determinations were in the proportions required by the stoichiometry of the equation for a weight of 1.42 g of C_3A . First the NC_8A_3 was dissolved in the calorimeter and the final rate of temperature rise determined to complete the measurement of its heat of solution. This final rate became the initial rate for the CaSO_4 experiment. The sample of anhydrite was introduced and the determination was completed. This procedure was followed also with a new acid charge for the products on the right side of the equation. Thus the final calorimeter solution for the measurements with the reactants was of the same composition as that for the products, and no dilution experiments were necessary. The experimentally determined energy equivalent of the calorimeter and acid charge was used in computing the heats of solution of NC_8A_3 and C_3A . For CaSO_4 and Na_2SO_4 it was increased by 0.28 cal/deg, the estimated heat capacity of the solid previously added. Since this increase was less than 0.1 percent of the total energy equivalent, the error introduced by this approximation was negligible.

¹ Figures in brackets indicate the literature references at the end of this paper.
² As usual in papers dealing with portland-cement compounds, the abbreviations C for CaO , A for Al_2O_3 , N for Na_2O , and H for H_2O will be used.

TABLE 1. Heats of solution in 425.0 g of HCl·26.61H₂O

Sample number	Na ₂ O·8CaO·3Al ₂ O ₃ (816.51) ^a		CaSO ₄ (136.15) ^a		3CaO·Al ₂ O ₃ (270.20) ^a		Na ₂ SO ₄ V(142.06) ^a	
	Sample weight	Heat of solution	Sample weight	Heat of solution	Sample weight	Heat of solution	Sample weight	Heat of solution
	<i>g</i>	<i>cal/g</i>	<i>g</i>	<i>cal/g</i>	<i>g</i>	<i>cal/g</i>	<i>g</i>	<i>cal/g</i>
1	1.4220	733.52	0.2415	-13.00	1.4200	736.43	0.2515	-32.43
2	1.4233	733.81	.2382	-12.88	1.4189	735.49	.2518	-33.02
3	1.4254	734.05	.2385	-12.36	1.4220	735.27	.2563	-32.82
4	1.4262	734.11	.2378	-12.83	1.4215	735.92	.2526	-32.66
5	1.4276	734.25	.2407	-12.32	1.4228	735.91	.2549	-32.35
Avg		733.95		-12.69		735.80		-32.66
S. D. ^b		0.13		0.14		0.19		0.12
-ΔH	<i>kcal/mole</i> 599.28±0.106		<i>kcal/mole</i> -1.728±0.019		<i>kcal/mole</i> 199.11±0.051		<i>kcal/mole</i> -4.640±0.017	

^a Numbers in parentheses are molecular weights. ^b Standard deviation of the average. ^c Corrected for C₃AH₆.

3. Heats of Solution

The results of the measurements of the heats of solution in hydrochloric acid are given in table 1. The negative sign before values in this table indicates that the heat of solution was endothermic. The value shown there for C₃A when corrected for the calculated C₂AH₆ impurity becomes 736.9 cal/g. This value, which was used in computation, may be compared with some previously obtained results. In 1930, Thorvaldson, Brown, and Peaker [2] obtained 736.0 cal/g³ for the heat of solution of 2.86 g of C₃A in 600.4 g of HCl, 20H₂O at 20° C. In 1939 Cirilli [7] obtained 735.1 cal/g for the heat of solution of C₃A in 3.5 N HCl at 25° C. Recently Coughlin [8] obtained 738.0 cal/g for the heat of solution of 1.43 g of C₃A in 1936.2 g of 4.360 M HCl at 30° C. These four values, including the one obtained in this work, are in reasonably good agreement.

No data were found in the literature on the heat of solution of sodium sulfate in hydrochloric acid. Two determinations in this laboratory with larger samples (1.42 g) than were used for the data in table 1 gave values of -32.38 and -31.87 cal/g, respectively.

Newman and Wells [5] obtained -12.75 cal/g for the heat of solution of CaSO₄ in HCl, 26.61H₂O, and Southard [9] obtained -12.28 cal/g in 2.03 N NCl. These values are in substantial agreement with those in table 1.

4. Heats of Formation

From the heats of solution in table 1, the heat for reaction 1 at 25° C is calculated to be ΔH₁ = +4.85 ± 0.19 kcal/mole. To determine the heat of formation of NC₃A₃ the heats of formation of the other three members of eq 1 must be known.

The heat of formation of C₃A is given as -861 kcal/mole in Circular 500 of the National Bureau of Standards [10]. This value was used in computations. Although Coughlin [8] gave the value -850.04 ± 1.23 or -853.46 ± 1.23 kcal/mole depending on the value used for the heat of combustion of calcium, these values appear to be low by 3.18 kcal, twice his value for the heat of formation of C₃A from the oxides.

³ The value given in 20° calories by Thorvaldson, et al., has been recalculated to the thermochemical calory of 4.1840 absolute joules used in this paper.

The heat of formation of Na₂SO₄ V was obtained by measuring its heat of solution in water to form Na₂SO₄·1000H₂O, the heat of formation of which is -331.215 kcal [10]. Five determinations gave -293.0 ± 2.9 cal/mole for the enthalpy of solution at 25° C. Coughlin's value at 30° C [11], -628.2 cal/mole, was calculated to be -302.2 cal/mole at 25° C. The heat of formation of Na₂SO₄ V was taken as -331.215 + 0.293 = -330.922 kcal/mole.

The heat of formation of CaSO₄, anhydrite, is -342.42 kcal/mole [10]. From these values for the heats of formation of C₃A, Na₂SO₄ V, and anhydrite, and the heat of reaction ΔH₁, the heat of formation of NC₃A₃ from the elements at 25° C is calculated to be -2576 kcal/mole.

5. Summary

The compounds 3CaO·Al₂O₃, Na₂SO₄ V (thenardite), Na₂O·8CaO·3Al₂O₃, and CaSO₄, anhydrite, were prepared, and their heats of solution in HCl, 26.61H₂O were determined. The heat of solution of Na₂SO₄ V in water to form Na₂SO₄·1000H₂O was also measured. From these and other data in the literature the heats of formation of Na₂O·8CaO·3Al₂O₃ and Na₂SO₄ V were calculated to be -2576 and -330.92 kcal/mole, respectively.

6. References

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WASHINGTON, March 18, 1958.