The enthalpies of formation and of dehydration of some AFm phases with singly charged anions

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THE ENTHALPIES OF FORMATION AND OF DEHYDRATION
OF SOME AFm PHASES WITH SINGLY CHARGED ANIONS*.

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ABSTRACT

The enthalpies of formation of some AFm phases of the type $\text{Ca}_2\text{Al}(\text{OH})_6\text{X} \cdot x\text{H}_2\text{O}$ ($\text{X} = \text{Cl}^-$, Br^- , I^- , NO_3^- , ClO_4^- , ClO_3^- , BrO_3^- and IO_3^-) were determined by measuring the heats of solution in hydrochloric or perchloric acid. From the differences between the heats of solution of the compounds and their dehydration products, the enthalpies of dehydration were established. They increase with increasing enthalpies of hydration of the individual anions X in aqueous solution. However, this relationship is not the same for halide ions as for oxy-anions.

Die Bildungsenthalpien einiger AFm Phasen $\text{Ca}_2\text{Al}(\text{OH})_6\text{X} \cdot x\text{H}_2\text{O}$ ($\text{X} = \text{Cl}^-$, Br^- , J^- , NO_3^- , ClO_4^- , ClO_3^- , BrO_3^- und IO_3^-) wurden bestimmt durch Messung der Lösungswärme dieser Verbindungen in HCl oder HClO_4 . Mittels der Differenzen zwischen den Lösungswärmen der hydratisierten und dehydratisierten Verbindungen wurden die Dehydratationsenthalpien festgestellt. Diese nehmen zu mit steigender Hydratationsenthalpie der individuellen Anionen X in wässriger Lösung; aber die Relation ist verschieden für Halogenionen und für Oxy-anionen.

*Part of the Ph.D. Thesis by C.J.M. Houtepen, Eindhoven 1975, and presented as a supplementary paper at the 6th International Congress on the Chemistry of Cement, Moscow 1974.

Introduction

A number of data concerning the enthalpies of formation of calcium aluminates and silicates have been published (1-13). These values are based partly on calculated, partly on experimentally determined quantities. Thus Babushkin and Mchedlov-Petrosyan (1) calculated the enthalpy of formation of C_4AH_{13} (-1983 kcal) making use of the contributions to this quantity from $Ca(OH)_2$, $Al(OH)_3$ and the lattice water. The contributions from $Ca(OH)_2$ and $Al(OH)_3$ to the enthalpy of formation were calculated from that of C_3AH_6 (-1317.6 kcal), on the supposition that this compound consists of $3Ca(OH)_2 \cdot 2Al(OH)_3$, and from the enthalpy of formation of C_2AH_5 ($2Ca(OH)_2 \cdot 2Al(OH)_3$), -1078 kcal (11). Such calculations may be justified in some cases, but in others they lead to large errors. Thus the enthalpy of formation of C_3AH_6 calculated from that of C_3A (8) using an approximate general relationship for the enthalpy of hydration of anhydrous compounds (14, 15) is -1283.5 kcal, but the experimental value is -1326 kcal (8). Clearly there is a need for experimental data.

The AFm compounds of general formula $Ca_2Al(OH)_6X \cdot xH_2O$ have almost identical crystal structures, which are essentially unaffected by removal of the interlayer water (16-18). Dehydration causes mainly a decrease of the layer thickness c and is reversible as long as the dehydration conditions are not too severe. The question is whether any relationship exists between the enthalpies of dehydration of these compounds and the enthalpies of hydration of the individual anions X . For the clay minerals such as montmorillonite and vermiculite, the cations located in the interlayers have an important effect on the ability to accommodate interlayer water (19-21); the enthalpies of dehydration of these clay minerals depend on the enthalpies of hydration of the cations in aqueous solution. In the AFm phases anions might play a similar role.

Preparation and Characterization

Samples were prepared by the following methods:

- a. To a suspension of C_3A (2.7 g) in 2-propanol (50 ml), prepared as described by De Jong (22), was added a solution of 50 to 100 mmoles $CaX_2 \cdot zH_2O$ in CO_2 -free water (500 ml). The 2-propanol was used to prevent a too rapid hydration of C_3A . The reaction mixture was magnetically stirred for at least five days at room temperature. The precipitate was filtered off, washed with a methanol-water mixture followed by a methanol-acetone mixture, and dried over saturated $CaCl_2 \cdot 6H_2O$ (37% relative humidity) in a vacuum desiccator.
- b. C_3AH_6 was prepared by heating C_3A (2.7 g) in water (250 ml) at $175^\circ C$ in an autoclave for 120 hours, as described by Thorvaldson (2).
- c. " C_4AH_{13} " was prepared at $0^\circ C$ by adding a solution of sodium aluminate to a saturated solution of calcium hydroxide in such a way that the Ca/Al ratio in the solution was always greater than two. This method is analogous to that employed by Buser (23).
- d. Samples of $Ca_2Al(OH)_6NO_3 \cdot xH_2O$ were prepared by a method analogous to method a, but about $175^\circ C$ in an autoclave, resulting in larger crystals.
- e. The iodate compound was prepared as described by Le Bel and Grasland (18).

In all preparations precautions were taken against carbonation. The water used was distilled twice at reduced pressure. Filtration was performed in a CO₂-free glove box. All samples were analysed chemically. Table I gives the compositions of the samples and their dehydration products; despite the precautions taken some carbonation usually occurred. The samples and dehydration products were also characterized by X-ray diffraction, care being taken to exclude CO₂ and H₂O by covering the samples with "Mylar" foil. For the hydrated phases no differences were found between X-ray diffraction patterns made with and without such a foil, except for C₄AH₁₃. The hemicarboxate phase with layer thickness 8.2 Å was absent, but the 7.9 Å reflection had a shoulder on the low-angle side and chemical analysis (Table I) showed that CO₂ was present. In general the layer thicknesses found for the AFm phases and their dehydration products agreed with those in the literature (17, 18). Results of interest were for the hydrated chlorate compound, 9.30 Å; for the dehydrated nitrate, 7.28 Å; and for the dehydrated bromate, 8.36 Å. All molar quantities used in this paper relate to formulae of the type Ca₂Al(OH)₆X.xH₂O.

Heat of Solution Measurements

The heats of solution of the AFm phases were determined in HCl (1N or 2N) or in perchloric acid (1N) at 25°C with a precision calorimeter, LKB 8700-1 (24). The heats of solution were calculated using the graphical extrapolation method of Dickinson (25, 26). The calorimeter was calibrated electrically and chemically by measuring the heat of solution of CaO, prepared by burning CaCO₃ (Merck p.a.) at 1100°C for several hours. $\Delta H_{\text{soln.}}$ was found to be -46.7 ± 0.3 kcal mole⁻¹ which implies $\Delta H_f^\circ \text{CaO, c} = -151.9 \pm 0.3$ kcal mole⁻¹, in agreement with literature data (10). For accurate determinations the heat of dilution caused by the disappearance of the acid and the formation of water on dissolution of the samples must be taken into account. It can, however, be proved that, if the amount of sample (0.2 mmole) is small compared with the amounts of acid (80 mmoles) and of water (4.5 mole), the heat of dilution is negligible. The enthalpy of dehydration i.e. the change of enthalpy involved in the hypothetical reaction:

was determined as the difference between the heats of solution of the dehydrated and the hydrated compounds. This procedure is justified because, if equimolar amounts of the hydrated compounds are dissolved, the final states of the resulting solutions are nearly the same.

Enthalpies of Formation

The enthalpies of formation of the AFm phases were determined from heats of solution in HCl using the following reaction scheme:

The enthalpy of formation is then:

$$\begin{aligned} \Delta H_f^\circ \text{Ca}_2\text{Al}(\text{OH})_6 \cdot y\text{X} \cdot 0.5(1-y)\text{CO}_3 \cdot x\text{H}_2\text{O} &= 2 \Delta H_f^\circ [\text{CaCl}_2, n_4/2\text{H}_2\text{O}] \\ &+ \Delta H_f^\circ [\text{AlCl}_3, n_4\text{H}_2\text{O}, n_3\text{HCl}] + y \Delta H_f^\circ [\text{X}, n_4/y\text{H}_2\text{O}] - y \Delta H_f^\circ [\text{HCl}, n_4/y\text{H}_2\text{O}] \\ &+ 0.5(1-y) \Delta H_f^\circ \text{CO}_2(\text{aq}) - n_2 \bar{H}_1(\text{H}_2\text{O}) - n_1 \bar{H}_1(\text{HCl}) + n_4 \bar{H}_2(\text{H}_2\text{O}) \\ &+ n_3 \bar{H}_2(\text{HCl}) - \Delta H_{\text{soln.}} \end{aligned} \quad (2)$$

$\Delta H_f^\circ [\text{CaCl}_2, n_4/2\text{H}_2\text{O}]$ is the enthalpy of formation of one mole CaCl_2 in $n_4/2$ mole H_2O . $\bar{H}_1(\text{H}_2\text{O})$ and $\bar{H}_2(\text{H}_2\text{O})$ are the partial molar enthalpies of water in solutions of one mole H_2O with n_1/n_2 mole HCl or n_3/n_4 HCl , respectively. $\bar{H}_1(\text{HCl})$ and $\bar{H}_2(\text{HCl})$ are the partial molar enthalpies of HCl in solutions of one mole HCl with n_2/n_1 and n_4/n_3 mole H_2O respectively. The enthalpy of formation of AlCl_3 in aqueous solution depends strongly on the water and HCl concentrations (12). This enthalpy was found by interpolation of literature data (12) $\Delta H_f^\circ [\text{AlCl}_3, 200\text{HCl}, 11000\text{H}_2\text{O}] = -245.7 \text{ kcal mole}^{-1}$. The other data were taken from literature (8,12,13). In the calculations, thermochemical data for CO_2 dissolved in water have been used (12). This may be questionable in view of the small solubility of CO_2 in 1N HCl . However, the difference between the enthalpies of formation of CO_2 in aqueous solution and in the gas phase is too small to have any noticeable influence on the calculations.

If the heat of solution in perchloric acid was measured, the enthalpy of formation was established as follows:

$$\begin{aligned} \Delta H_f^\circ \text{Ca}_2\text{Al}(\text{OH})_6 \cdot y\text{X} \cdot 0.5(1-y)\text{CO}_3 \cdot x\text{H}_2\text{O} &= -\Delta H_{\text{soln.}} + \\ 2\Delta H_f^\circ [\text{Ca}^{2+}, n_4/2\text{H}_2\text{O}] + \Delta H_f^\circ [\text{Al}^{3+}, n_4\text{H}_2\text{O}] &+ y\Delta H_f^\circ [\text{X}, n_4/y\text{H}_2\text{O}] + \\ 0.5(1-y)\Delta H_f^\circ \text{CO}_2(\text{aq}) + (n_4-n_2)\Delta H_f^\circ [\text{H}_2\text{O}, n_3/n_4\text{HClO}_4] \end{aligned} \quad (3)$$

$$\Delta H_f^\circ [\text{Ca}^{2+}, n_4/2\text{H}_2\text{O}] = \Delta H_f^\circ [\text{CaCl}_2, n_4/2\text{H}_2\text{O}] - 2\Delta H_f^\circ [\text{HCl}, n_4/4\text{H}_2\text{O}] \quad (4)$$

$$\Delta H_f^\circ [\text{Al}^{3+}, n_4\text{H}_2\text{O}] = \Delta H_f^\circ [\text{AlCl}_3, n_4\text{H}_2\text{O}] - 3\Delta H_f^\circ [\text{HCl}, n_4/3\text{H}_2\text{O}] \quad (5)$$

Discussion

A. The Heats of Solution and the Enthalpies of Formation

The heats of solution of the $\text{Ca}_2\text{Al}(\text{OH})_6\text{X}_x \cdot x\text{H}_2\text{O}$ compounds are nearly independent of X , if $x = 2$ and $\text{X} = \text{Cl}^-$, Br^- , I^- , NO_3^- , ClO_4^- or ClO_3^- (Table I). If $x > 2$ ($\text{X} = \text{BrO}_3^-$, IO_3^-) the heats of solution decrease with increasing amount of interlayer water. With increasing carbonation the heat of solution increases, since the heat of solution of $\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.5\text{CO}_3 \cdot 2.39\text{H}_2\text{O}$ is -63.7 kcal (5) which is relatively large. The heat of solution of the iodide compound containing 0.03 mole % CO_2 differs about 1 kcal from that of the almost CO_2 -free compound (Table I). The heat of solution of $\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.92\text{OH} \cdot 0.04\text{CO}_3 \cdot 3\text{H}_2\text{O}$ (-76.9 kcal) differs considerably from those of the other AFm phases. The heat of solution of pure $\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.3\text{H}_2\text{O}$ (-78 kcal) was established by

extrapolation, assuming a linear relation between the heats of solution of $\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.92\text{OH} \cdot 0.04\text{CO}_3 \cdot 3\text{H}_2\text{O}$ and of $\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.5\text{CO}_3 \cdot 2.39 \text{H}_2\text{O}$. The heats of solution of the dehydration products can be correlated with the interaction energies between the anions X and the $\text{Ca}_2\text{Al}(\text{OH})_6$ -layers (27). We can conclude from equation 2 that, if $x = 2$, the enthalpies of formation of $\text{Ca}_2\text{Al}(\text{OH})_6 \cdot x \cdot \text{H}_2\text{O}$ ($X = \text{Cl}^-, \text{Br}^-, \text{J}^-, \text{NO}_3^-, \text{ClO}_4^-$ and ClO_3^-) can be expressed by the equation:

$$\Delta H_f^\circ \text{Ca}_2\text{Al}(\text{OH})_6 \cdot x \cdot 2\text{H}_2\text{O} = -874 (\pm 1) + \Delta H_f^\circ [X, 10.000\text{H}_2\text{O}] \quad (6)$$

This means that the lattice enthalpies of these AFM phases depend linearly on the enthalpies of hydration of the anions X concerned.

$$\begin{aligned} \text{For: } \Delta H_{\text{lattice}} &= \Delta H_f^\circ [\text{Ca}_2\text{Al}(\text{OH})_6^+, g] + \Delta H_f^\circ [X, g] + 2\Delta H_f^\circ [\text{H}_2\text{O}, g] \\ &- \Delta H_f^\circ \text{Ca}_2\text{Al}(\text{OH})_6 \cdot x \cdot 2\text{H}_2\text{O} \end{aligned} \quad (7)$$

The $\text{Ca}_2\text{Al}(\text{OH})_6^+$ -ion in the gas phase is an hypothetical ion. From equation 6 and 7 follows:

$$\Delta H_{\text{lat.}} = C_1 + \Delta H_f^\circ (X^-, g) - \Delta H_f^\circ (X^-, \text{aq}) = C_1 - \Delta H_{\text{hydr.}} (X^-, g) \quad (8)$$

$$\text{since } \Delta H_{\text{hydr.}} (X^-, g) = \Delta H_f^\circ (X^-, \text{aq}) - \Delta H_f^\circ (X^-, g) \quad (9)$$

The enthalpy of formation of pure Ca_4Al_3 , calculated from the heat of solution, $-156 \text{ kcal mole}^{-1}$ and the enthalpies of formation of the reactants is -1988 kcal . Babushkin calculated -1983 kcal ; the agreement is in this case very satisfactory. But if we calculate the enthalpy of formation of e.g. $\text{Ca}_2\text{Al}(\text{OH})_6 \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$ by the method of Babushkin, supposing that the hydrate consists of $1.5 \text{ Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and $0.5 \text{ CaCl}_2 \cdot 4\text{H}_2\text{O}$ we get -899 kcal . The experimental value is -914 kcal . This difference occurs because the surroundings of the ions in the AFM phases differ from those in $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, to extents that apparently cannot be neglected.

B. The Enthalpies of Dehydration

In Fig.1 the enthalpies of dehydration of the AFM phases are given together with the absolute enthalpies of hydration of the anions X. For the halide ions, the hydration enthalpies were calculated from the enthalpies of formation in the gas state and the "absolute" enthalpies of formation in aqueous solution. The "absolute" enthalpies of formation are related to the conventional enthalpies of formation (tabulated in the literature) by the equation:

$$\Delta H_f^\circ (X, \text{aq})_{\text{abs.}} = \Delta H_f^\circ (X, \text{aq})_{\text{conv.}} - \Delta H_f^\circ (\text{H}^+, \text{aq})_{\text{abs.}} \quad (10)$$

$$\text{where } \Delta H_f^\circ (\text{H}^+, \text{aq})_{\text{abs.}} = 95.6 \text{ kcal mole}^{-1} (\text{ref. 30}).$$

The enthalpies of dehydration of the AFM phases are linearly related to the enthalpies of hydration of the anions X (Fig.1).

For the oxy-anions, the hydration enthalpies are not known precisely, because the enthalpies of formation of the gaseous

TABLE I

Analytical and thermochemical results

Chemical composition	prep. method	mmoles	$-\Delta H_{\text{soln.}}$ kcal	$-\Delta H_f^0$ kcal
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.92\text{OH} \cdot 0.04\text{CO}_3 \cdot 3.0\text{H}_2\text{O}$	c	0.3924	76.9	993
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.96\text{NO}_3 \cdot 0.02\text{CO}_3 \cdot 2.0\text{H}_2\text{O}$	d	0.4238	61.0	992
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.96\text{NO}_3 \cdot 0.02\text{CO}_3$	f	0.3982	67.7	
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.98\text{ClO}_4 \cdot 0.01\text{CO}_3 \cdot 2.1\text{H}_2\text{O}$	a	0.4416	60.9	910
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.98\text{ClO}_4 \cdot 0.01\text{CO}_3$	f	0.3841	66.2	
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 1.00\text{Cl} \cdot 2.1\text{H}_2\text{O}$	a	0.4092	62.0	917
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 1.00\text{Cl}$	f	0.4171	72.0	
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.96\text{Br} \cdot 0.02\text{CO}_3 \cdot 2.1\text{H}_2\text{O}$	a	0.4074	60.9	913
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.96\text{Br} \cdot 0.02\text{CO}_3$	f	0.4084	70.5	
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.94\text{I} \cdot 0.03\text{CO}_3 \cdot 2.1\text{H}_2\text{O}$	a	0.3585	61.6	894
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.94\text{I} \cdot 0.03\text{CO}_3$	f	0.3801	69.2	
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 1.00\text{I} \cdot 2.0\text{H}_2\text{O}$	a	0.4038	60.5	887
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 1.00\text{I}$	f	0.4131	68.3	
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.98\text{ClO}_3 \cdot 0.01\text{CO}_3 \cdot 2.1\text{H}_2\text{O}$	a	0.4139	60.9*	904
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.98\text{ClO}_3 \cdot 0.01\text{CO}_3$	f	0.4113	68.7*	
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.98\text{BrO}_3 \cdot 0.01\text{CO}_3 \cdot 2.8\text{H}_2\text{O}$	a	0.3916	58.6*	950
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 0.98\text{BrO}_3 \cdot 0.01\text{CO}_3$	f	0.3909	70.0*	
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 1.00\text{IO}_3 \cdot 4.1\text{H}_2\text{O}$	e	0.3395	53.4*	1074
$\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 1.00\text{IO}_3$	f	0.3389	72.3*	
C_3AH_6	b	0.2311	139.1	1326

*For measuring the heats of solution of AFm phases with oxy-anions incorporated, HClO_4 (1N) was used. f = dehydration product.

FIG. 1

The enthalpies of dehydration of some compounds of general formula $\text{Ca}_2\text{Al}(\text{OH})_6\text{X} \cdot x\text{H}_2\text{O}$ plotted against the "absolute" hydration enthalpies of the individual anions X in aqueous solution. Numerical values of the quantities are given on the right.

TABLE II

X^-	$\Delta H_{\text{hydr.}}$	$-\Delta H_{\text{hydr.}}$
IO_3^-	18.9	97.6
BrO_3^-	11.4	79.3
ClO_3^-	10.0	76.7
ClO_4^-	7.8	72.9
Br^-	9.6	68.7
NO_3^-	6.7	67.1
ClO_4^-	5.3	65.9
I^-	7.8	61.8

ions cannot be determined experimentally. The most reliable way of estimating them seems to be that first proposed by Morris (28), which is based on the hypotheses that the salting-out of lyophilic colloids by electrolytes is determined by the hydration enthalpies of the ions present (29). The salting-out properties of an anion, expressed as a "lyotropic number", can be measured for both halides and oxy-anions; assuming that the same relation between enthalpy of hydration and lyotropic number applies for halides and oxy-anions, the hydration enthalpies of the oxy-anions are known. Hydration enthalpies thus obtained are shown in Fig.1. As for the halides a linear relationship is found, but the points for the oxy-anions do not lie in the same curve as those for the halides. This is ascribed to differences in the sizes and chemical characteristics of the two kinds of ion.

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