The dehydration of some calcium aluminate hydrates, with univalent anions

Citation for published version (APA):

Houtepen, C. J. M., & Stein, H. N. (1976). The dehydration of some calcium aluminate hydrates, with univalent anions. *Journal of Colloid and Interface Science*, 56(2), 370-376. [https://doi.org/10.1016/0021-9797\(76\)90264-2](https://doi.org/10.1016/0021-9797(76)90264-2)

DOI:

[10.1016/0021-9797\(76\)90264-2](https://doi.org/10.1016/0021-9797(76)90264-2)

Document status and date:

Published: 01/01/1976

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

The Dehydration of Some Calcium Aluminate Hydrates, with Univalent Anions

C. J. M. HOUTEPEN AND H. N. STEIN

Laboratory of General Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

Received August 31, 1975; December 12, 1975

The enthalpy of removing interlayer water of the calcium aluminate hydrates of the type $2(\text{Ca}_2\text{Al}(\text{OH})_6^+\text{X}^-\cdot y\text{H}_2\text{O})$ ($y=2$, if $\text{X}^-=\text{Cl}^-$, Br^- , I^- , NO_3^- , ClO_3^- , ClO_4^- ; $2 < y < 4$ if $\text{X}^-=\text{BrO}_3^-$, JO_3^- at 37% relative humidity and room temperature) is related to the enthalpy of hydration of the anion X^- .

The enthalpy of dehydration of the hydrates cannot be determined as isosteric heat of adsorption from dehydration or rehydration temperatures as a function of the water vapor pressure because the dehydrated compound cannot be regarded as an inert adsorbent in the process of hydration.

The enthalpy of dehydration of the compounds can be calculated as the sum of some quantities including the electrical energy required to displace the anions and the enthalpy of partial hydration of the anions concerned in the gaseous state.

INTRODUCTION

One type of calcium aluminate hydrate consists of main layers $\text{Ca}_2\text{Al}(\text{OH})_6^+$ alternated by interlayers in which anions are surrounded by water molecules (1-4). The type of anions to be incorporated can vary widely; in the present investigation only univalent anions have been considered.

Lavanant (5) examined the dehydration and rehydration of some of these calcium aluminate hydrates as a function of temperature and water vapor pressure and, in spite of the occurring hysteresis, he used the Clausius-Clapeyron equation to establish the enthalpy of dehydration. It is questionable whether this is correct, because the dehydration is irreversible in the thermodynamic sense. One of the objects of our investigation (6-8) on the calcium aluminate hydrates was the comparison of the enthalpies of dehydration, determined both calorimetrically and by measuring dehydration and rehydration temperatures at different water vapor pressures in order to obtain more insight into the

process of dehydration (hydration) of the compounds mentioned.

EXPERIMENTAL

The calcium aluminate hydrates were prepared and analyzed as described previously (6, 7). The enthalpies of dehydration were determined by measuring the enthalpies of solution of the hydrated and the dehydrated compounds in 1 *N* HCl or 1 *N* HClO₄ (7) in an LKB 8700-1 precision calorimeter. If small amounts (about 0.2 mmoles) of the sample are dissolved in about 84 ml hydrochloric acid (1 *N*), the heat of dilution caused by the formation of water on dissolution of the calcium aluminate hydrate is negligible. Moreover, if we dissolve about the same amount of the dehydrated and the hydrated compound, the difference of the heats of solution per mole calcium aluminate hydrate gives directly the enthalpy change of the reaction:

which is by definition the enthalpy of dehydration, ΔH_{deh} .

Dehydration and rehydration of the compounds were followed thermogravimetrically by means of a micro balance, C.I. Electronics type Mark II, equipped with a so-called universal attachment in order to maintain a controlled atmosphere above the sample. A constant water vapor pressure was maintained by passing an air flow, after circulation through potassium hydroxide solutions of known concentration, over the sample. The relative humidity of the air at 20°C was measured by means of an hygrometer (Hygro-dynamics Inc.) calibrated with relative humidities above saturated solutions of various salt hydrates (9). A thermogram of the dehydration of $2[\text{Ca}_2\text{Al}(\text{OH})_6^+X^-\cdot 2\text{H}_2\text{O}]$ ($X^- = \text{Br}^-, \text{ClO}_4^-$) was composed by raising the temperature in steps of 5 or 1°C, waiting at each temperature 5 to 24 hr until no or no further weight loss was observed. The "dehydration temperature", t_D , was defined as the temperature at which the dehydration, as measured by the procedure described, has advanced for 50%. A similar definition was used for the rehydration temperature, t_R .

RESULTS

The enthalpies of dehydration of the calcium aluminate hydrates found calorimetrically are given in Table I, column a. The dehydration and rehydration temperatures found thermogravimetrically at different relative humidities (r) of the atmosphere above the sample are given in Table II for the compound with $X^- = \text{Br}^-$. If we apply the Clausius-Clapeyron equation to this data, the apparent enthalpy of dehydration " ΔH " follows from the linear relation between $\log(r)$ and $1/T_D$ (T_D = dehydration temperature in Kelvin); " ΔH " = 71 ± 5 kJ/mole H_2O . ΔH , the real enthalpy of dehydration corresponding to the process occurring in the thermobalance is connected with ΔH_{deh} , as defined by Eq. [1],

TABLE I

The Enthalpies of Dehydration of the Calcium Aluminate Hydrates $2[\text{Ca}_2\text{Al}(\text{OH})_6^+X^-\cdot y\text{H}_2\text{O}]$ ($y = 2$ if $X^- = \text{ClO}_4^-, \text{NO}_3^-, \text{Cl}^-, \text{Br}^-, \text{J}^-$, and ClO_3^- ; $2 < y < 4$ if $X^- = \text{BrO}_3^-, \text{JO}_3^-$); the Enthalpies of Hydration of the Individual Anions in Aqueous Solution and Their Lyotropic Number

X^-	^a ΔH_{deh} (kJ/mole hydrate)	^b $-\Delta H_{\text{hydr}}$ (X^- , g)abs (kJ/gr ion)	^c Lyotropic number (N)
JO_3^-	159.8	408.3	6.25
BrO_3^-	95.8	331.8	9.55
Cl^-	83.3	320.9	10.00
Br^-	77.8	287.4	11.3
ClO_3^-	64.9	305.0	10.65
J^-	64.0	258.6	12.5
NO_3^-	54.0	280.7	11.6
ClO_4^-	44.8	275.7	11.8

as follows:

$$n \cdot \Delta H = \Delta H_{\text{deh}} + \int_{298}^T \Delta C_p \cdot dT + n \cdot \Delta H_{\text{L} \rightarrow \text{G}}(\text{H}_2\text{O}) \quad [2]$$

($n = 4$ in the case $X^- = \text{Br}^-$, at room temperature and 37% relative humidity), where ΔC_p is the difference between the heat capacities of n mole $\text{H}_2\text{O}(\text{g})$ together with one mole of the dehydrated calcium aluminate hydrate and the heat capacity of the hydrated compound; $\Delta H_{\text{L} \rightarrow \text{G}}(\text{H}_2\text{O})$ is the enthalpy of evaporation of one mole H_2O at temperature t_D .

If we assume $\Delta C_p = 0$, it follows from Eq. [2] with $\Delta H_{\text{L} \rightarrow \text{G}}(\text{H}_2\text{O}) = 42.05$ kJ/mole and the ΔH_{deh} -value of the calcium aluminate hydrate concerned as given in Table I,

TABLE II

The Dehydration- and Rehydration Temperatures of the Reactions: $2[\text{Ca}_2\text{Al}(\text{OH})_6^+\text{Br}^-\cdot 2\text{H}_2\text{O}]$ (s) $\rightleftharpoons 2[\text{Ca}_2\text{Al}(\text{OH})_6^+\text{Br}^-]$ (s) + $4\text{H}_2\text{O}(\text{g})$

Relative humidity (%) at 20°C	t_D (°C)	t_R (°C)
19	69.2	60.0
30	75.0	67.2
55	83.2	74.3
70	88.0	79.0

$\Delta H = 61 \pm 2$ kJ/mole H_2O . Similarly, for the hydrate containing ClO_4^- , in this way $\Delta H = 53 \pm 2$ kJ/mole H_2O is found. The " ΔH "-values are respectively 71 ± 5 and 65 ± 5 kJ/mole H_2O . The difference between the values obtained calorimetrically and from rehydration or dehydration temperatures distinctly surpasses the experimental error.

DISCUSSION

(a) Comparison of the Enthalpies of Dehydration Determined Calorimetrically and by Thermogravimetry

The application of the Clausius-Clapeyron equation on dehydration and rehydration temperatures at different water vapor pressures is suspect because of lack of equilibrium (cf. the occurring hysteresis). However, at any temperature the relationship $\ln p_{\text{deh}} \leq \ln p_{\text{equil}} \leq \ln p_{\text{rehydr}}$ will hold; thus it is probable that:

$$\left(\frac{\partial \ln p}{\partial (1/T)} \right)_{\text{deh}} \geq \left(\frac{\partial \ln p}{\partial (1/T)} \right)_{\text{equil}} \geq \left(\frac{\partial \ln p}{\partial (1/T)} \right)_{\text{reh}}$$

(if this relationship would not hold, then a rehydration equilibrium establishment would be particularly good at low temperatures, which is very improbable). Since

$$\left(\frac{\partial \ln p}{\partial (1/T)} \right)_{\text{reh}} = \left(\frac{\partial \ln p}{\partial (1/T)} \right)_{\text{deh}},$$

this would be an argument for identifying both with

$$\left(\frac{\partial \ln p}{\partial (1/T)} \right)_{\text{eq}}.$$

The difference between the values for ΔH_{deh} found calorimetrically and thermogravimetrically cannot be ascribed to differences in degree of crystal perfection. It is true the former includes all crystals present in the sample (even very small or partially disordered ones), whereas the latter may reasonably be thought to be restricted mainly to well-ordered crystals, but $\partial \ln p / \partial (1/T)$ -values are only slightly dependent on the degree of

dehydration or rehydration (6). Thus the fact that the isosteric heat of dehydration as calculated from thermogravimetric results is a differential heat, whereas calorimetry yields the integral heat, cannot be accepted as explanation for the observed discrepancy. Rather it should be realized that the isosteric heat of dehydration as found from $\partial \ln p / \partial (1/T)$ -slopes only coincides with the real dehydration enthalpy (ΔH) as defined in Eq. [2], if the dehydrated compound may be regarded as an inert adsorbent in the process of hydration. Formally, the calcium aluminate hydrate may be treated as a solid solution of variable water content (10). The enthalpy change of the reaction:

where

is equal to:

$$\begin{aligned} &h(\text{H}_2\text{O}, \text{g}) + (1/n)h_A \\ &+ H(\text{H}_2\text{O}, B) - (1/n)H(A, B) \quad [4] \\ &(A \cdot n\text{H}_2\text{O} = B) \end{aligned}$$

$h(\text{H}_2\text{O}, \text{g})$ = the enthalpy of one mole H_2O in the gas phase

$H(\text{H}_2\text{O}, B)$ = the partial molar enthalpy of one mole H_2O in the crystal hydrate considered as solid solution

$H(A, B)$ = the partial molar enthalpy of one mole of the dehydrated compound in the crystal hydrate considered as solid solution.

By measuring the dehydration temperature as function of the water vapor pressure we determine the difference between the enthalpy of water in the gaseous state and the partial molar enthalpy of water in the crystal hydrate:

$$\begin{aligned} &[\partial \ln p / \partial T]_n \\ &= (h(\text{H}_2\text{O}, \text{g}) - H(\text{H}_2\text{O}, B)) / RT^2. \end{aligned}$$

From calorimetry, on the other hand, we find (after taking into account the enthalpy of

vaporization of the water) per mole of water
 $\Delta H = -(1/n)h(B) + (1/n)h(A) + h(\text{H}_2\text{O}, \text{g})$.

Treating again the calcium aluminate hydrate as a solid solution of variable water content we can replace $h(B)$ by $H(A, B) + nH(\text{H}_2\text{O}, B)$. Thus:

$$\Delta H = -(1/n)H(A, B) - H(\text{H}_2\text{O}, B) + (1/n)h(A) + h(\text{H}_2\text{O}, \text{g})$$

which will be identical with $[\partial \ln p / \partial (1/T)]_n$ only when $H(A, B) = h(A)$, i.e., when A may be regarded as an inert adsorbent.

From our data we can conclude that h_A is a more negative quantity than the partial molar enthalpy $H(A, B)$. This means that during hydration of $2[\text{Ca}_2\text{Al}(\text{OH})_6^+X^-]$ part of the enthalpy change is required for changing the "adsorbent." The occurring hysteresis can be explained by comparing the calcium aluminate hydrates with the analogous clay minerals like montmorillonite, vermiculite a.o. (11, 12).

(b) *Comparison of the Enthalpies of Dehydration of Calcium Aluminate Hydrates Containing Different Anions*

The enthalpies of dehydration (ΔH_{deh}) of the calcium aluminate hydrates, as determined calorimetrically, increase in the sequence

It was expected that there should be a relation between ΔH_{deh} of $2[\text{Ca}_2\text{Al}(\text{OH})_6^+X^- \cdot y\text{H}_2\text{O}]$ and the enthalpies of hydration, ΔH_{hydr} , of the anions X^- . For $X^- = \text{halide ions}$, ΔH_{hydr} is known from Born-Haber cycle (13); however, for $X^- = \text{oxy-anions}$ the calculation concerned cannot be carried out since the enthalpies of formation of the anions in the gaseous state are not known. ΔH_{hydr} for oxy-anions is often calculated by methods (13-17) involving cationic and anionic radii. However, these radii are in general not uniquely defined (cf. the existence of very different sets of ionic radii such as those of Pauling, Goldschmidt, Waddington, Gourary and Adrian);

in addition, the consideration of oxy-anions as spherical anions is not realistic and the dimensions of an anion depend strongly on the electric field (18) exerted by surrounding ions, which makes the use of one ionic radius for an anion in different solids and in the gas phase doubtful.

We therefore estimated ΔH_{hydr} of the oxy-anions by the method proposed by Morris (19) and Waddington (17). It is based on the existence of a linear relation between the enthalpy of hydration and the so-called "lyotropic number" (20-22) in those cases where both can be measured (halide ions); for oxy-anions only the lyotropic number can be established. This can be used to estimate ΔH_{hydr} by assuming that the same linear relation between ΔH_{hydr} and the lyotropic number is valid for oxy-anions as for halide ions. Since the lyotropic number is connected with the Gibbs free energy of hydration rather than with ΔH_{hydr} (6), the assumption mentioned is identical with the hypothesis that at a given enthalpy of hydration, the entropy of hydration is fixed, and that the relation between them is the same for oxy-anions and for halide ions.

"Absolute" enthalpies of hydration have been calculated (Table I, column b), defined by:

$$\Delta H_{\text{hydr}}(X^-, \text{g})_{\text{abs}} = \Delta H_f^0(X^-, \text{aq})_{\text{abs}} - \Delta H_f^0(X^-, \text{g}) \quad [5]$$

$$\Delta H_f^0(X^-, \text{aq})_{\text{abs}} = \Delta H_f^0(X^-, \text{aq})_{\text{conv}} - \Delta H_f^0(\text{H}^+, \text{aq})_{\text{abs}}. \quad [6]$$

Here $\Delta H_f^0(X^-, \text{aq})_{\text{conv}}$ is the "conventional" enthalpy of formation of X^- in aqueous solution as found in the literature (see, e.g., (23)); $\Delta H_f^0(\text{H}^+, \text{aq})_{\text{abs}} = 400 \text{ kJ gramion}^{-1}$ (15).

In Fig. 1, the enthalpies of dehydration of the calcium aluminate hydrates are shown versus $\Delta H_{\text{hydr}}(X^-, \text{g})_{\text{abs}}$. Two linear relations with different slopes are found; moreover, the enthalpies of dehydration of the calcium aluminate hydrates are only 10-15% of the enthalpies of hydration of the anions concerned.

In order to understand this, the process of

FIG. 1. The enthalpies of dehydration of the calcium aluminate hydrates $2[\text{Ca}_2\text{Al}(\text{OH})_6^+\text{X}^-\cdot y\text{H}_2\text{O}]$ versus the "absolute" enthalpies of hydration of the individual anions X^- in aqueous solution.

hydration of a calcium aluminate hydrate $2[\text{Ca}_2\text{Al}(\text{OH})_6^+\text{X}^-]$ is divided into two hypothetical steps:

(a) the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ -layers and X^- ions are displaced to their final positions (in the hydrated compound) without water being taken up,

(b) water is introduced at constant inter-layer distance.

The enthalpy required by step (a) comprises an electrostatic term (ΔE) and the enthalpy required for overcoming non-Coulombic interaction between X^- and the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ layers (ΔH_{I}). ΔE can be esti-

mated by van Olphen's method (11): the negative charge of the anions X^- is thought to be smeared out in a plane through the middle of the interlayer, the positive charge of the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ -layers thought to be placed in a plane midway of these layers. So the crystal lattice is considered as a number of plate condensers. We obtain

$$\Delta E = 2\pi\sigma^2\Delta c \cdot 2N_{\text{Av}} \cdot A/\epsilon, \quad [7]$$

$\Delta c = c - c'$ = change of the basal basing on dehydration (cm); σ = charge density of the hypothetical surfaces = $e/28.63 \cdot 10^{16}$ esu cm^{-2} ; $e = 4.803 \cdot 10^{-10}$ esu; N_{Av} = Avogadro number; A = the surface of a unit cell (3); ϵ = effective dielectric constant (estimated to be 6, based on dielectric constants of comparable solid compounds). The differences of the basal spacings as determined by X-ray diffraction (6), Δc , and ΔE values are given in Table III.

The enthalpy change of process "b" may be compared with the enthalpy of anion X^- in aqueous solution, provided the fact is taken into account that water molecules in the crystal lattice have as their nearest neighbors fixed hydroxyl groups (as distinguished from water molecules in a dilute solution).

We will take into account this fact by two correction quantities, ΔH_{II} and ΔH_{III} .

TABLE III

The Difference in the Electrostatic Interaction Energy of the Anions X^- with the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ -Layers When they are Displaced over a Distance Δc Away from the Main Layers

X^-	Δc (6) (nm)	ΔE ($\epsilon = 6$) (kJ/mole hydrate)
Cl^-	0.096	97.1
Br^-	0.102	102.9
J^-	0.120	120.9
NO_3^-	0.132	133.9
ClO_3^-	0.112	113.4
BrO_3^-	0.144	145.6
JO_3^-	0.185	184.9
ClO_4^-	0.142	143.5

ΔH_{II} represents the enthalpy change on account of the interaction of the water molecules with the hydroxyl groups of the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ -layers on introducing water into $\text{Ca}_2\text{Al}(\text{OH})_6^+X^-$ previously brought to distance (step "a"). ΔH_{III} represents the enthalpy change on disrupting water to water bonds in dilute solution.

The enthalpy of hydration of a calcium aluminate hydrate can then be expressed by the equation:

$$\Delta H_{\text{hydr}}(\text{complex}) = \Delta E + \Delta H_I + \Delta H_{II} + \Delta H_{III} + 2\Delta H_{\text{hydr}}(X^-, g)_{\text{abs}} \quad [8]$$

It is reasonable to assume that the sum of $\Delta H_{II} + \Delta H_{III}$ is constant (independent of the type of anion). So the different slopes of the curves drawn in Fig. 1 are caused by the contribution of ΔH_I . It means that the hydrogen bonds between the anions and the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ -layers in the dehydrated crystal lattice differ more in the case of the halides than in the case of the oxy-anions. The sum of $\Delta H_I + \Delta H_{II} + \Delta H_{III}$ is rather large compared with the enthalpy of hydration of the calcium aluminate hydrate, even after taking into account the electrostatic energy required for the displacement of the anions away from the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ -layers. However, it makes

perhaps more sense to compare the enthalpies of hydration of the hydrates with the enthalpies of partial hydration of anions X^- in the gaseous state.

Recently some data about those enthalpies were published by Arshadi, Kebarle, Payzant *et al.* (24-27). The enthalpy of hydration of the calcium aluminate hydrate can then be expressed by the equation

$$\Delta H_{\text{hydr}}(\text{complex}) = \Delta E + 2 \cdot \Delta H_{0,2}(X^-, g) + \Delta H_I + \Delta H_{II} \quad [9]$$

In Fig. 2 the separate contributions are shown. It appears that the enthalpy of hydration of the calcium aluminate hydrate is nearly equal to $2\Delta H_{0,2}(X^-, g) + \Delta E$ (taking into account the uncertainty in the quantity ΔE because of the estimated value for $\epsilon (=6)$). This is true, also in the case $X^- = \text{NO}_3^-$. For the other anions a comparison is not possible since no data about the partial hydration enthalpies are available.

CONCLUSION

During the hydration of the dehydrated calcium aluminate hydrates $2[\text{Ca}_2\text{Al}(\text{OH})_6^+X^-]$ part of the enthalpy change is required to change the "absorbent." The enthalpy of

FIG. 2. Δ , $\otimes$: $-\Delta H_{\text{deh}}(\text{hydrate})$; $\times$: $2 \cdot \Delta H_{\text{hydr}}(X^-, g)_{\text{abs}}$; $\square$, $\odot$: $2 \cdot \Delta H_{\text{hydr}}(X^-, g)_{\text{abs}} + \Delta E$; $\oplus$: $2\Delta H_{0,2}(X^-, g)$; $\ominus$: $2\Delta H_{0,2}(X^-, g) + \Delta E$.

hydration of the compounds mentioned can be calculated from the enthalpy of partial hydration of the anion X^- in the gaseous state after correcting for the enthalpy required to displace the anion X^- over a certain distance away from the main layers.

The enthalpies of dehydration (hydration) of the compounds cannot be established by measuring the dehydration or rehydration temperatures at different water vapor pressures because of lack of equilibrium. Moreover, the apparent enthalpy of dehydration determined with the Clausius-Clapeyron equation is only the difference of the molar enthalpy of water vapor and the partial molar enthalpy of water intercalated in the calcium aluminate hydrate and does not include the enthalpy required to change the "adsorbent" during the process of hydration or rehydration.

ACKNOWLEDGMENT

We thank Mr. C. L. M. Holten, Mr. J. P. M. van Seters, and Mr. F. E. A. M. B. Lemmerling for carrying out the experiments.

REFERENCES

- FEITKNECHT, W., AND BUSER, H., *Helv. Chim. Acta* **34**, 128 (1951).
- AHMED, S., AND TAYLOR, H. F. W., *Nature (London)* **215**, 622 (1967).
- KUZEL, H., in "Proc. 5th Intern. Symp. Chem. Cement, Tokyo 1968," Suppl. paper II-19, Vol. II, p. 92.
- LE BEL, F., AND GRASLAND, G., in "Proc. 5th Intern. Symp. Chem. Cement, Tokyo 1968," Vol. II, p. 79.
- LAVANANT, F., *Revue des Matériaux de Construction* **592**, 1 (1965); **593**, 76; **595**, 193; **596**, 251; **597**, 298.
- HOUTEPEN, C. J. M., Ph.D. Thesis, Technological University Eindhoven, Eindhoven, 1975 (in Dutch).
- HOUTEPEN, C. J. M., AND STEIN, H. N., in "6th Intern. Congress Chem. Cement, Moscow 1974," supplementary paper Section II.
- HOUTEPEN, C. J. M., AND STEIN, H. N., *Spec-trochimica Acta*, to be published.
- FELDMAN, R. F., AND RAMANCHANDRAN, V. S., *Thermochim. Acta* **2**, 393 (1971).
- YOUNG, D. M., AND CROWELL, A. D., "Physical Adsorption of Gases," Butterworths, London, 1962.
- VAN OLPHEN, H., *J. Colloid Sci.* **20**, 822 (1965).
- SPOSITO, G., AND BABCOCK, K. L., in "Proc. 14th National Conference on Clay and Clay Minerals 1966," p. 133.
- LADD, M. F. C., AND LEE, W. H., in "Progress in Solid State Chemistry" (H. Reiss Ed.), Vol. I, Chapter II. MacMillan, New York 1964.
- DESNOYERS, J. E., AND JOLICOEUR, C., in "Modern Aspects of Electrochemistry" (J. O. M. Bockris and B. E. Conway Eds.), Vol. 5, Chapter I. Plenum, New York, 1969.
- ROSSEINSKY, D. R., *Chem. Rev.* **65**, 467 (1965).
- HALLIWELL, H. F., AND NYBURG, S. C., *Trans. Faraday Soc.* **59**, 1126 (1963).
- WADDINGTON, T. C., in "Advances in Inorganic Chemistry and Radiochemistry" (H. J. Emeleus and A. G. Sharpe Eds.), Vol. I, p. 158. Academic Press, New York, 1959.
- JOHNSON, O., *Inorg. Chem.* **12**, No. 4 780 (1973).
- MORRIS, D. F. C., *J. Inorg. Nucl. Chem.* **6**, 295 (1958).
- VOET, A., *Chem. Rev.* **20**, 169 (1937).
- BRUINS, E. M., *Proc. Acad. Sci. Amsterdam* **35**, 107 (1932); *Rec. Trav. Chim. Pays-Bas* **53**, 292 (1934).
- BÜCHNER, E. H., *Kolloid Zeitschr.* **75**, 1 (1936).
- "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-3, U.S. Government Printing Office, Washington D.C. 20402.
- ARSHADI, M., KEBARLE, D., SCARBOROUGH, J., *J. Chem. Phys.* **49**, 817 (1968).
- ARSHADI, M., YAMDAGNI, R., AND KEBARLE, P., *J. Phys. Chem.* **74**, 1475 (1970).
- PAYZANT, J. D., YAMDAGNI, R., AND KEBARLE, P., *Canad. J. Chem.* **49**, 3308 (1971).
- YAMDAGNI, R., PAYZANT, J. D., AND KEBARLE, P., *Canad. J. Chem.* **51**, 2507 (1973).