THERMOANALYTICAL AND CALORIMETRIC INVESTIGATIONS ON THE FORMATION AND DECOMPOSITION OF SOME ALUNITES *

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(Received 8 November 1986)

ABSTRACT

Under hydrothermal conditions the formation of oxonium alunite (OxAl) and potassium alunite (KAl) was experimentally determined as a function of temperature. The straight lines $\ln K = f(T)$ obtained are the result of the experiments described. From the calorimetric determination of the thermal capacity, the standard formation enthalpy and the standard entropy, $\ln K = f(T)$ functions could be calculated. Comparison of experimental and calculated results has proved to be satisfactory for KAl, where the non-stoichiometry is the main consideration. The agreement is not very good for OxAl because of foreign phase components. Investigation of the thermal decomposition under quasi-isothermal and quasi-isobaric conditions shows that the alunites have a defined decomposition temperature. Reactions preceding this decomposition are due to the loss of excess water.

INTRODUCTION

Alunites are basic sulphates of the ideal composition $MeAl_3(SO_4)_2(OH)_6$, where $Me = K^+$, Na^+, NH_4^+, H_3O^+, etc. The non-stoichiometry compared with the ideal composition is typical of the basic sulphates. It is mainly characterized by excess water in the structure and a deficiency of Al^{3+} ions [1,2]. Moreover, the numerous isomorphic relations on the Me sites as well as between other basic sulphates, such as jarosite, are of great interest.

The formation of the basic sulphates from solutions, especially under hydrothermal conditions, and their thermal stability are of particular interest due to their application in the separation and cleaning stages of technological processes and in the hydrothermal formation of geological deposits.

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

Potassium alunite, $KAl_3(SO_4)_2(OH)_6$ (KAl), and oxonium alunite, $H_3OAl_3(SO_4)(OH)_6$ (OxAl), form the subject of the present investigation. The differences in the properties of the two alunites with identical crystal structures are essentially based on the different ionic radii of the K^+ and H_3O^+ ions, respectively.

The crystal structure of alunites and isomorphic jarosites involves an optimum ionic radius of the Me ion which is obviously best satisfied by the K^+ ion. Deviations from this optimum result in a decreased formation affinity from aqueous solutions and a decreased thermal stability.

Whereas the equilibrium of jarosite formation and derivation of the thermodynamic reaction quantities has been repeatedly investigated [3], analogous results concerning the formation of alunite are not available. In the present paper the thermodynamics of formation of potassium and oxonium alunites from aqueous solutions are investigated by determining the equilibrium concentration above the solid phase with respect to temperature. They are calculated on the basis of calorimetric measurements of standard formation enthalpy, standard entropy and thermal capacity of the two alunites. Comparison of the results is satisfactory.

Thermal decomposition of the alunites under dynamic conditions has often been investigated and discussed [4,5]. The quasi-isothermal and quasi-isobaric conditions of thermal decomposition used in the present work lead to more definite statements, mainly relating to the decomposition temperature of the alunites and the influence of excess water in the structure.

EXPERIMENTAL

Synthesis and investigation of the equilibrium of potassium alunite were carried out in the temperature range 373–438 K. Potassium and aluminium sulphate solutions ($c_{Al} = 0.15$ mol l^{-1}) were converted under hydrothermal conditions in closed reaction vessels using five times the excess of potassium used in the stoichiometric approach in order to prevent the formation of oxonium alunite. Investigations of the formation of oxonium alunite from pure aluminium sulphate solutions were performed in the temperature range 453–513 K. The solid phase could be separated from the solution under equilibrium conditions. Chemical analyses of the solid phase and the equilibrium solution were carried out as follows: aluminium, complexometric method; sulphate as $BaSO_4$, gravimetric method; and potassium, flame-photometric method. The following formula was used to characterize the composition and to express the non-stoichiometry:
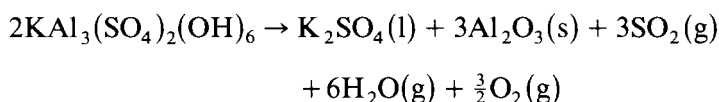
$$MeAl_x(SO_4)_2(OH)_{3x-3}(H_2O)_y$$
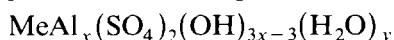
Exact determination of x and y on the basis of the chemical analysis is an important prerequisite to the accuracy of the subsequent thermodynamic calculations. The errors obtained were 0.01 for x and 0.04 for y.
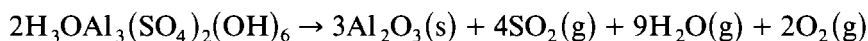
Since synthetically produced potassium alunites usually show a striking non-stoichiometry, a natural alunite (deposit from Beregszasz, Hungary) was used for calorimetric investigations, of ideal composition within the error range given.

A low-temperature calorimeter [6] was used to determine the thermal capacity and the standard entropy, which allowed measurements on the basis of the isoperibolic method between 20 and 300 K. Thermal capacity values were obtained at 0–20 K by extrapolation on the basis of the T^3 law.

As the basic salts are only slightly soluble, solution calorimetry cannot be used to determine the formation enthalpy of alunites. An appropriate method is high-temperature drop calorimetry using the 1500°C high-temperature calorimeter manufactured by Setaram, France [7]. The dropped samples totally decompose at an operating temperature of 1573 K according to

$$2KAl_3(SO_4)_2(OH)_6 \rightarrow K_2SO_4(l) + 3Al_2O_3(s) + 3SO_2(g)$$

$$+ 6H_2O(g) + \tfrac{3}{2}O_2(g)$$

and

$$2H_3OAl_3(SO_4)_2(OH)_6 \rightarrow 3Al_2O_3(s) + 4SO_2(g) + 9H_2O(g) + 2O_2(g)$$

The initial temperature of the samples was 298 K. The measured enthalpy change, ΔH_{298}^T, corresponds to the sum of the decomposition enthalpy $\Delta_R H_{298}^\ominus$ at 298 K and the enthalpy change of the reaction products when increasing the temperature from 298 K to the measuring temperature, T:

$$\Delta_R H_{298}^\ominus = \Delta H_{298}^T - \Sigma \nu_i \int_{298}^{T} C_{p_i} \, dT$$

where i indicates decomposition products. Finally, the formation enthalpy of the sample can be calculated by means of the known formation enthalpies of the decomposition products $\Delta_B H_{i,298}^\ominus$ and the value of $\Delta_R H_{298}^\ominus$:

$$\Delta_B H_{298}^\ominus(\text{alunite}) = -\Delta_R H_{298}^\ominus + \Sigma \nu_i \Delta_B H_{298,i}^\ominus$$

The advantage of this method is that the thermodynamic standard values can be evaluated immediately since mixing effects are excluded and the gaseous reaction products are formed at low partial pressures and high temperatures. The accuracy of the method is ±2%, but an error of ±0.6% results for the formation enthalpy $\Delta_B H_{298}^\ominus$ (alunite).

The thermal decomposition of the alunites was followed by means of the Q-type derivatograph (MOM, Budapest) under quasi-isothermal and quasi-isobaric conditions [8]. In addition to a weight loss, with selected samples the release of SO_3 could be determined separately with a titrimeter coupled to the apparatus.

RESULTS

The precipitation equilibrium for the formation of alunites of ideal stoichiometric composition must be defined as

$$Me^+(aq) + 3Al^{3+}(aq) + 2SO_4^{2-}(aq) + 6H_2O(l)$$

$$\rightleftarrows MeAl_3(SO_4)_2(OH)_6 + 6H^+(aq)$$
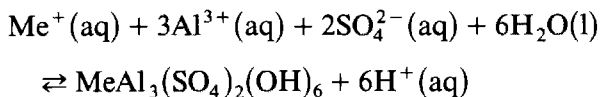
The equilibrium was calculated from analytical values of the solid phase and the equilibrium solution under the following conditions. (1) Concentrations were used instead of the mean activity coefficients of the ions since the latter are not readily available under the test conditions. Consequently, the calculated equilibrium constant is the conventional constant K_c. (2) The real composition of the basic salts could be considered in the definition and calculation of the equilibrium.

A linear correlation between $\ln K_c$ and T^{-1} was taken as a basis for the temperature dependence of the equilibrium constants. For a mean investigation temperature, the reaction enthalpy $\Delta_R H(\overline{T})$ is obtained from the slope of the straight line and $\Delta_R S(\overline{T})$ from the intercept. Figure 1 shows the correlations between $\ln K_c$ and T^{-1} for potassium alunite and oxonium alunite. The linear correlation is satisfied very well and, consequently, there is no problem in calculating with the concentrations instead of the activities.

The measuring temperature applied during drop calorimetry was kept as high as possible so that the sulphate decomposes completely to give SO_2 and O_2 (Tables 1 and 2). The resulting error in the formation enthalpy of the alunites (± 30 kJ mol^{-1}) is relatively high for thermodynamic calculations.
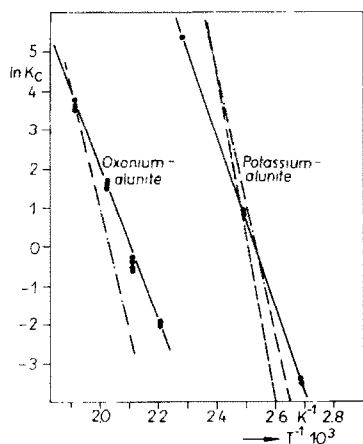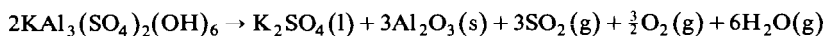

Fig. 1. Equilibrium of OxAl, and KAl. ($\bullet$——$\bullet$) Experimental values; (– · · –) OxAl, calculated for $H_3OAl_{3.03}(SO_4)_2(H_2O)_{0.61}$; (— —) KAl, calculated for $KAl_3(SO_4)_2(OH)_6$; (· – · – ·) KAl, calculated for $KAl_{2.46}(SO_4)_2(OH)_{4.38}(H_2O)_{2.3}$.

TABLE 1

Determination of the formation enthalpy for potassium alunite (C_p and $\Delta_F H_{298}^{\ominus}$ values from ref. 9, values are given in kJ mol^{-1})

$$2KAl_3(SO_4)_2(OH)_6 \rightarrow K_2SO_4(l) + 3Al_2O_3(s) + 3SO_2(g) + \tfrac{3}{2}O_2(g) + 6H_2O(g)$$

	$\int_{298}^{1573} C_p dT$	$\Delta_F H_{298}^{\ominus}$
$Al_2O_3(s)$	151.98	-1675.7
$H_2O(g)$	51.79	-241.814
$SO_2(g)$	66.36	-296.810
$O_2(g)$	43.29	0
$K_2SO_4(s, l)$	287.02	-1437.700

$\Sigma \nu_i \int C_{p_i} dT = 1317.7 \quad \Sigma \nu_i \Delta_B H_i^{\ominus} = -8806.12$

$\Delta H_{298}^T = 2564.4$ [a]

$\Delta_R H_{298}^{\ominus} = 1246.7 \quad \Delta_F H_{298}^{\ominus} = -5026.4 \pm 30$

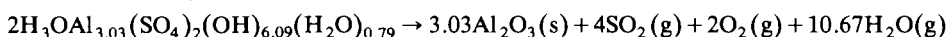[a] Mean value of six measurements, ± 30 kJ mol^{-1}.

As shown by the following equilibrium calculations, the uncertainty caused by the non-stoichiometry of the alunites has a far greater influence. Calculation of the equilibrium constants was carried out on the basis of the following relation:

$$RT \ln K = -\Delta_R H_{298}^{\ominus} + T\Delta_R S_{298}^{\ominus} + T\left(\ln \frac{T}{298} + \frac{298}{T} - 1\right)\Delta_R C_{p,298}^{\ominus}$$

The initial values for the calculation of $\Delta_R H_{298}^{\ominus}$, $\Delta_R S_{298}^{\ominus}$ and $\Delta_R C_{p,298}^{\ominus}$ are

TABLE 2

Determination of the formation enthalpy of oxonium alunite (C_p and $\Delta_F H_{298}^{\ominus}$ values from ref. 9, values are given in kJ mol^{-1})

$$2H_3OAl_{3.03}(SO_4)_2(OH)_{6.09}(H_2O)_{0.79} \rightarrow 3.03Al_2O_3(s) + 4SO_2(g) + 2O_2(g) + 10.67H_2O(g)$$

	$\int_{298}^{1476} C_p dT$	$\int_{298}^{1501} C_p dT$	$\Delta_F H_{298}^{\ominus}$
$Al_2O_3(s)$	139.09	142.23	-1675.7
$H_2O(g)$	46.66	47.75	-241.814
$SO_2(g)$	60.72	61.12	-296.810
$O_2(g)$	39.24	40.10	0

$\Sigma \nu_i \int C_{p_i} dT = 1240.6 \quad \Sigma \nu_i \int C_{p_i} dT = 1296.2 \quad \Sigma \nu_i \Delta_B H_i^{\ominus} = -8856.4$

$\Delta H_{298}^T = 2891.4$ [a] $\quad \Delta H_{298}^T = 2953.1$ [a]

$\Delta_R H_{298}^{\ominus} = 1668.9 \quad \Delta_R H_{298}^{\ominus} = 1702.6 \quad \Delta_F H_{298}^{\ominus} = -5261.9 \pm 30$

[a] Mean value of three measurements, ± 30 kJ mol^{-1}.

TABLE 3

Thermodynamic values for calculating the equilibrium

	$\Delta_F H_{298}^{\ominus}$ (kJ mol^{-1})	$S_{298}^{\ominus}$ (J K^{-1} mol^{-1})	$C_{p,298}^{\ominus}$ (J K^{-1} mol^{-1})
Al^{3+}	− 525.5 [11]	− 301 [11]	372.6 [13]
SO$_4^{2-}$	− 909.6 [10]	18.83 [10]	− 481.5 [13]
H$^+$	0	0	117.2 [13]
H$_2$O(l)	− 285.83 [10]	69.95 [10]	75.78 [13]
K$^+$	− 252.17 [10]	101.04 [10]	129.8 [13]
KAl	− 5026.4	480.5 [12]	441.2 [13]
OxAl	− 5261.9	353.2 [12]	428.9 [13]

given in Table 3. The stoichiometry of the precipitation reaction has a considerable influence on the result. Table 4 compares experimental and calculated values. There is a large difference in the reaction quantities $\Delta_R H$ and $\Delta_R S$, which are strongly dependent on the stoichiometry. From Fig. 1, however, the position of the equilibrium curves is in good agreement for potassium alunite, whereas this is only true of a mean non-stoichiometry in the case of oxonium alunite. Plots of temperature versus molar thermal capacity for potassium alunite and oxonium alunite are given in Figs. 2 and 3. At ~ 240 K the uniform curves show traces of an anomaly which might be connected with an excess of water. There are no indications of a change in the bonding state of this water from electrical conductivity measurements and H NMR spectra [14]. The standard entropies from the molar heat capacity curves are given in Table 3.

TABLE 4

Comparison of experimental and calculated values

Potassium alunite	Exp.	Calc. for KAl(SO$_4$)(OH)$_6$	Calc. for KAl$_{2.46}$(SO$_4$)$_2$- (OH)$_{4.38}$(H$_2$O)$_{2.3}$
$\Delta_R H^{\ominus}$ (403 K)	185	378.9	285.4
$\Delta_R S^{\ominus}$ (403 K)	468	947.2	725.04
ln K (373 K)	− 3.36	− 8.83	− 5.32
ln K (438 K)	5.49	10.04	9.00

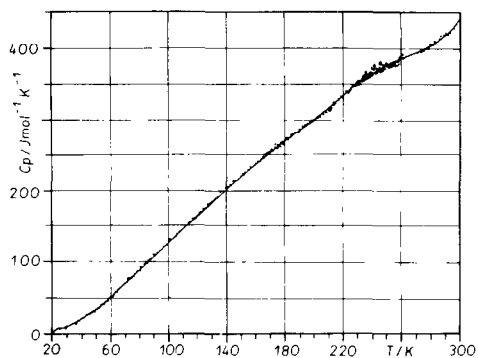| Oxonium alunite	Exp.	Calc. for H$_3$OAl$_3$(SO$_4$)(OH)$_6$	Calc. for H$_3$OAl$_{3.03}$(SO$_4$)$_2$- (OH)$_{6.09}$(H$_2$O)$_{0.61}$
$\Delta_R H_T^{\ominus}$ (483 K)	225.4	195.6	401.6
$\Delta_R S_T^{\ominus}$ (483 K)	471.1	888.1	822.3
ln K (473 K)	− 0.5	57.1	− 3.18
ln K (513 K)	3.75	61.0	3.75

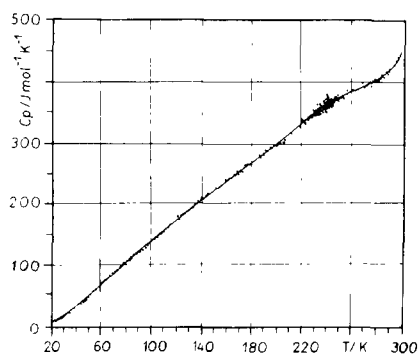Fig. 2. Molar heat capacity versus T for OxAl.

Fig. 3. Molar heat capacity versus T for KAl.

Derivatographic curves of the thermal decomposition of three alunite samples are shown in Figs. 4–6. Four characteristic temperatures can be derived, the values of which are given in Table 5. The non-stoichiometric influence is clearly visible. The excess water of potassium alunite is released
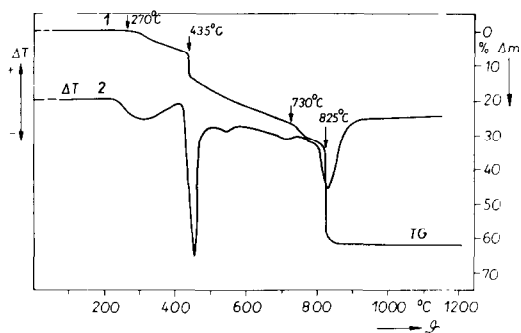

Fig. 4. Derivatographic curves for OxAl: (1) Q–TG curve, (2) ΔT curve.
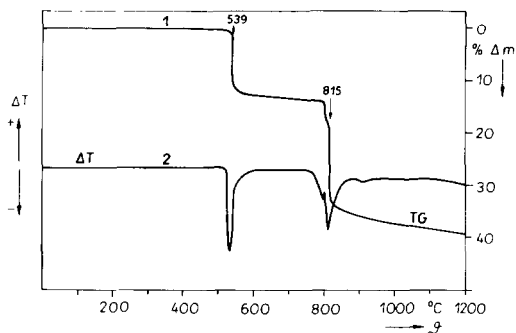
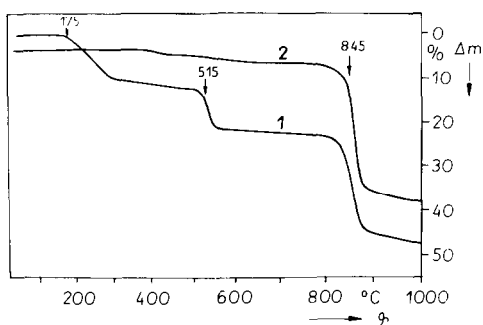Fig. 5. Derivatographic curves for KAl (stoichiometric): (1) Q–TG curve, (2) ΔT curve.

Fig. 6. Derivatographic curves for KAl [$KAl_{2.35}(SO_4)_2(OH)_{4.05}(H_2O)_{2.3}$]: (1) Q–TG curve, (2) titration curve.

in one step from 175 to ~ 250°C. As evident from X-ray diffraction patterns of thermally treated samples, the structure of the alunites is largely maintained. The real decomposition takes place in a nearly isothermal step at 435°C for oxonium alunite and 539°C for potassium alunite, forming aluminium sulphate and aluminium oxide (transition alumina), respectively. These temperatures represent the real stability limit of the two alunites under near equilibrium conditions. In the case of KAl, potassium sulphate is

TABLE 5

Characteristic temperatures of the thermal decomposition for (A) $KAl_{2.35}(SO_4)_2(OH)_{4.05}$-$(H_2O)_{2.3}$, (B) $KAl_3(SO_4)_2(OH)_6$ and (C) $H_3OAl_{3.03}(SO_4)_2(OH)_{6.09}(H_2O)_{0.7}$ (values in °C)

	A	B	C
Beginning of loss of H_2O	175	–	270
Decomposition	515	539	435
Beginning of loss of SO_3	390	785	730
Step of SO_3 loss	845	815	825

also present. Previous discussions of the thermal decomposition were quite formal from the TG curve and did not consider the excess water present [4]. Release of SO_3 at ~ 800°C corresponds to the decomposition of aluminium sulphate, which proceeds between 730 and 840°C under the same experimental conditions.

DISCUSSION

Equilibrium investigation results of the formation of alunite from aqueous solutions show that potassium alunite is formed in preference to oxonium alunite. A temperature difference of ~ 80°C is necessary for comparable conversions. Since the crystal structures of OxAl and KAl are identical and the reaction mechanism, essentially the hydrolytic reaction of $Al(OH_2)_6^{3+}$ [2], should be the same as before, the difference in formation affinity must be associated with the specific properties of the K^+ and H_3O^+ ions, respectively. As previously mentioned, the different ionic radius of the ions of equal charge and the geometry of the ions also have some influence. The Me ion has a coordination number of 12, and the spherical symmetry of the K^+ ion is in good conformity with this coordination. On the other hand, according to Kubisz [1] the H_3O^+ ion has the shape of a flat pyramid. Although a rotation of the H_3O^+ ion in the alunite lattice cannot be excluded, a disturbance potential results from the asymmetric charge distribution of the H_3O^+ ions, which might cause a lower OxAl formation affinity. The same tendency is shown by the thermal stability. The decomposition temperature of KAl is ~ 100 K higher than that of OxAl. In spite of the endothermicity, the decomposition of OxAl at 435°C takes place with a surprisingly high velocity. This fact can be understood only by assuming that the decomposition is connected with the reaction of OH^- and H_3O^+ ions to H_2O (inner neutralization), which proceeds very quickly.

A comparison of the experimental and calculated equilibrium curves (Table 4 and Fig. 1) shows quite good agreement for KAl, but an unsatisfactory result for OxAl. It is surprising that the position of the equilibrium curve for KAl is only weakly dependent on the non-stoichiometry. However, it must be taken into account that this non-stoichiometry is shown by a clear deficiency of Al^{3+} ions compared with the excess water in the structure. By varying the numbers of moles of Al and excess water so that the calculated equilibrium curve traces the experimental curve with minimum error, a nearly linear correlation is found between the deficiency of Al^{3+} ions and the excess of water. As shown in Fig. 7, the calculated correlation gives a good description of the experimentally determined composition of the potassium alunites. The different compositions of the potassium alunites are a result of the different synthesis temperatures, where the non-stoichiometry is reduced with increasing temperature. There is a large minimum in the
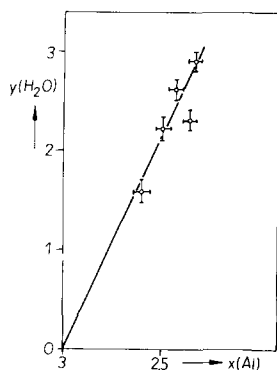
Fig. 7. Correlation of the H_2O/Al non-stoichiometry for KAl $[KAl_x(SO_4)_2(OH)_{3-x}(H_2O)_y]$: (———) calculated, (○) experimental.

dependence of the $\Delta_R G^\ominus$ function (isothermal) on this concrete non-stoichiometry. Hence, the formation of non-stoichiometric KAl is clear from the thermodynamic point of view. An attempt to correlate the temperature dependence of the non-stoichiometry and the minimum of the $\Delta_R G^\ominus$ function would be speculative, because the thermodynamic data are not precise enough.

The unusual stoichiometry is a starting point for explaining the unsatisfactory agreement of the calculated and experimental equilibrium constants (Fig. 1) in the case of OxAl. In contrast to other basic sulphates of the alunite/jarosite type, an excess of Al^{3+} ions apparently results in OxAl. This is difficult to explain on the basis of the structure of alunite. Therefore, it must be assumed that in addition to OxAl, a foreign phase with a higher Al/SO_4 ratio is formed. This foreign phase might be basaluminite of overall composition $2\ Al_2O_3 \cdot SO_3 \cdot xH_2O$ ($x = 10$–15) [15]. Even low portions of this phase, which cannot be detected by X-ray and other methods, involve a considerable error in the determination of thermodynamic values and above all in the thermodynamic calculations. Therefore, the results given for OxAl are only approximate, whereas those for KAl were confirmed by the experimental equilibrium investigations and can be used for other calculations, such as for energy balances or considerations of isomorphism.

Tests failed to obtain an OxAl with the expected non-stoichiometry by varying the synthesis temperature (180–250° C) and the initial concentration of aluminium sulphate ($0.05 \leq c_{Al} \leq 0.75$ mol l^{-1}). In each case a solid phase with an excess of aluminium was formed corresponding to the stoichiometric OxAl. Therefore, we do not consider it possible to carry out thermodynamic equilibrium calculation on OxAl. However, the precision of the determined values should be sufficient for the preparation of energy balances.

REFERENCES

1 J. Kubisz, Pol. Akad. Nauk, Pr. Mineral., 11 (1968) 7.
2 C. Härtig, P. Brand and K. Bohmhammel, Z. Anorg. Allg. Chem., 508 (1984) 159.
3 G. Hladky and E. Slansky, Bull. Mineral., 104 (1981) 468.
4 J. Pysiak and A. Glinka, Thermochim. Acta, 44 (1981) 21, 29, 101.
5 J. Kubisz, Polonica, 2 (1971) 51.
6 G. Wolf, Dissertation B, Freiberg, G.D.R., 1971.
7 R. Naumann and D. Petzold, J. Therm. Anal., 20 (1981) 319.
8 J. Paulik and F. Paulik, in G. Svehla (Ed.), Comprehensive Analytical Chemistry, Vol. XII, Part A, Elsevier, Amsterdam, 1981.
9 B.P. Gluschko, Thermodynamische Eigenschaften Individueller Stoffe, Nauka, Moscow, 1979.
10 Codata, J. Chem. Thermodyn., 10 (1978) 903.
11 V. Vasiljev, Eigenschaften von Electrolytlösungen, Vyzshaiascola, Moscow, 1982.
12 M. Thalheim, Diplomarbeit, B.A., Freiberg, G.D.R., 1984.
13 M.C. Criss and J.W. Cobble, J. Am. Chem. Soc., 86 (1964) 5385.
14 K. Bohmhammel and P. Brand, Z. Anorg. Allg. Chem., 542 (1986) 207.
15 E.V. Margulis, Z. Neorg. Chim., 29 (1984) 899.