Determination of equilibrium quantities of the systems formed by thermal decomposition according to the reaction
$$A(cond) \quad \rightleftarrows \quad B(cond) + C(g)$$

II. Divariant equilibrium states at thermal dehydration of CaC_2O_4 H_2O

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Temperature dependence of composition of solid phase coexisting in equilibrium with water vapour in the system formed at thermal dehydration of CaC_2O_4 H_2O was determined by isobaric-isothermal method. Temperature was changed in the range 80 °C—360 °C, the partial pressure of water vapour was kept at the values 7.6 kPa, 22.9 kPa, and 85.2 kPa, respectively. It was found that in the region of dehydration or rehydration of substantial amount of water the equilibrium composition of solid phase changes fluently with temperature while the partial pressure of water vapour remains constant. Thus the equilibrium is divariant and the coexisting phases are solid solution of CaC_2O_4 with CaC_2O_4 H_2O and water vapour.

When the composition of the solid solution was close to CaC_2O_4 H_2O we observed at dehydration or rehydration formation of the sequence of divariant equilibrium states with relatively constant composition of solid phase. Narrow temperature intervals corresponding to constant composition of solid phase moved with increasing pressure of water vapour to higher temperatures. It is assumed that this corresponds to gradual successive liberation or fixation of water molecules in different nonequivalent positions in the structure of solid solution. Relative distribution of water molecules bound in different positions in the structure of solid solution depends on temperature and pressure of water vapour.

The enthalpy of dehydration of solid solution determined from the slope of the dependence of equilibrium pressure of water vapour on reciprocal temperature does not depend on composition of the solid solution in the region of dehydration of main part of water and it equals $\Delta H_{deh} = (69.8 \pm 3)$ kJ mol^{-1}

In papers [1, 2] a method for determination of equilibrium data in the systems consisting of condensed phases and a gas phase has been proposed. In this work the above method is applied to the system CaC_2O_4—H_2O. We will present the

results of determination of equilibrium temperatures and corresponding equilibrium pressures of water vapour in the system formed at the thermal dehydration of CaC_2O_4 H_2O. Further, the character of equilibrium states as it follows from the determination of degrees of freedom of the system is discussed. The tensimetric determination of the enthalpy of dehydration of CaC_2O_4 H_2O and comparison of the results obtained by the static method with the literature data obtained by nonisothermal methods is presented.

Crystal structure of whewellite CaC_2O_4 H_2O was determined by X-ray diffraction and by spectroscopic methods [3—10]. There are, however, some discrepancies between these results. According to *Tazzoli* and *Domeneghetti* [7] the basic structure pattern of CaC_2O_4 H_2O is formed by the layers parallel with the plane (100). These layers are filled with Ca atoms and with a part of oxalate groups. The Ca atoms occupy vertexes of hexagons which have in their centres planar oxalate groups. Thus in the coordination sphere of calcium there are seven oxygen atoms belonging to the oxalate groups and one atom belonging to the molecule of water. The layers are bound by the remaining oxalate groups and molecules of water. The interlayer oxalate groups combined by pairs of water molecules form bands in the plain (010). These layers and bands form a system of tunnels parallel with axis C. Bonding between molecules of water and oxygen atoms in the interlayer oxalate groups as well as between the pairs of water molecules is made by hydrogen atoms.

Deganello [8, 9] claims that CaC_2O_4 H_2O exists in two polymorphic forms. High-temperature form (space group $I2/m$) is stable at the temperatures higher than 318 K, the low-temperature form (space group $P2_1/n$) is stable below this temperature. The transformation at 318 K is reversible. Stability of the high-temperature form is influenced by molecules of water which play two roles. They act as ligands and complete the coordination sphere of calcium and simultaneously they stabilize the structure by hydrogen bonds.

On the basis of Raman spectroscopic data *Duval* and *Condrate* [10] confirmed the order-disorder ($P2_1/n$—$I2/m$) polymorphic phase transition of CaC_2O_4 H_2O. According to these authors both forms of the monohydrate can coexist in the temperature range 273—376 K.

Dehydration of CaC_2O_4 H_2O

Gérard et al. [11—13] measured the equilibrium temperatures of dehydration of CaC_2O_4 H_2O and rehydration of CaC_2O_4, as a function of the pressure of water vapour. They simultaneously recorded temperature, DTA curves, and X-ray pattern at constant pressure of water vapour. Changes in temperature were slow. They considered the investigated system as monovariant. They found

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the standard enthalpy of the dehydration reaction to be $\Delta H° = (65.7 \pm 3)$ kJ mol^{-1} and standard entropy $\Delta S° = (121 \pm 13)$ J mol^{-1} K^{-1} They proved the existence of two polymorphic forms of CaC_2O_4 and determined the temperature of irreversible change of α-CaC_2O_4 into β form to be (182 ± 2) °C. They also found that liberation of water from monohydrate is a topotactic reaction accompanied with very small changes in interionic distances. At the thermal decomposition of CaC_2O_4 H_2O at pressure of water vapour lower than (12.0 ± 0.3) kPa a phase with the structure of α-CaC_2O_4 is obtained by fast transformation. This phase contains nonbound water. At further dehydration this water is removed from this phase. When the monohydrate is decomposed at higher pressure of water vapour than (12.0 ± 0.3) kPa a metastable α-CaC_2O_4 is formed in the first step. This metastable form spontaneously changes into the β form. However, the back transformation of β-CaC_2O_4 into α form does not proceed. In the region of stability of α-CaC_2O_4 the form β is changed directly at the rehydration to CaC_2O_4 H_2O. At the rehydration of β-CaC_2O_4 at pressures of water vapour higher than (12.0 ± 0.3) kPa a special phase with structure of β-CaC_2O_4 containing nonstoichiometric amount of water is formed. When the content of water reaches 1 mole per 1 mole of CaC_2O_4 this phase changes into CaC_2O_4 H_2O.

Shimizu and *Taniguchi* [14] measured the temperature dependence of equilibrium pressure of water vapour at dehydration of CaC_2O_4 H_2O in the temperature range 402—434 K by a transpiration method. They determined the standard enthalpy and entropy of the dehydration reaction to be $\Delta H° =$ $= (69.5 \pm 0.8)$ kJ mol^{-1} and $\Delta S° = (134.4 \pm 1.7)$ J mol^{-1} K^{-1} Also these authors considered the system formed by dehydration of CaC_2O_4 H_2O as monovariant.

Soustelle et al. [15] investigated different cases of divariant equilibria between water vapour and salt hydrates. They proposed two thermodynamic models of these equilibria. The first model assumes the existence of solid solution of "introduced" water in the salt. Thus water is an independent component in this model and it fills suitable interstitial positions in the structure of lower hydrate or anhydride. It has only negligible influence on the change of lattice parameters of the salt. Solid solution formed in this way can contain two types of water molecules which are nonequivalent from the crystallographic point of view. The enthalpy of dehydration is in this case close to the enthalpy of sublimation of water.

The second model assumes the existence of substitution solid solution of less hydrated salt in higher hydrate. This can happen under the condition that both components of the solid solution have similar structures. Water molecules occupy in the structure of solid solution the equivalent positions corresponding to one of the components. Change in the enthalpy of the dehydration reaction

according to this model is close to the value of this quantity for the monovariant dehydration.

In the paper [16], *Soustelle et al.* have shown that the course of isothermal function $\varepsilon(p)$ describing the equilibrium content of water in solid phase as a function of pressure of water vapour can be a suitable criterion for choice between the two proposed models and thus for determination of the nature of the solid solution. In the cited paper, possible boundaries of divariant regions in the system water vapour—hydrated salt are discussed.

Experimental

Preparation of sample

Sample of CaC_2O_4 H_2O was prepared by mixing of aqueous solutions of $CaCl_2$ and $(NH_4)_2C_2O_4$ of concentrations 0.5 mol dm^{-3} at ambient temperature. The precipitate was kept in contact with solution for 24 h at ambient temperature and for 24 h at the temperature of 90 °C. This procedure improved filtration of the product. Chlorides were removed by decantation, the precipitate was separated by filtration and dried at the temperature 100—105 °C. X-Ray diffraction and loss of mass at 200 °C and 1000 °C proved the quality of the product.

Principle of the method used

Temperature dependence of the composition of solid phase coexisting in equilibrium with water vapour was investigated using the apparatus which enables simultaneous isothermal heating of several solid samples at different temperatures and constant partial pressure of water vapour [1]. The equilibrium curves were obtained by interpolation of dissociation and association temperature dependences of mass losses of samples obtained at different times of isothermal heating. From the shape of the dependence of equilibrium composition of solid phase on temperature at given pressure of water vapour the number of degrees of freedom in the system can be determined [2].

Results and discussion

The dehydration and rehydration measurements were carried out at partial pressures of water vapour of 7.6 kPa, 22.9 kPa, and 85.2 kPa at temperatures in the range 80 °C—360 °C. Duration of experiments was 5 h, 24 h, and 71 h, respectively. Composition of solid phase after dehydration is given by relative mass losses calculated with respect to the initial mass of sample of CaC_2O_4 H_2O.

At the investigation of rehydration of CaC_2O_4, first the sample of anhydride CaC_2O_4 was prepared in the same apparatus which was used for dehydration measurement. On the basis of experimental data the following conditions for dehydration were chosen: temperature of 170—250 °C, partial pressure of water vapour 2.0 kPa, time 15 h. After rehydration the composition of solid phase was also expressed in relative losses of mass of sample related to the initial mass of CaC_2O_4 H_2O. Plot of relative mass losses *vs.* temperature results in curves similar to those for dehydration.
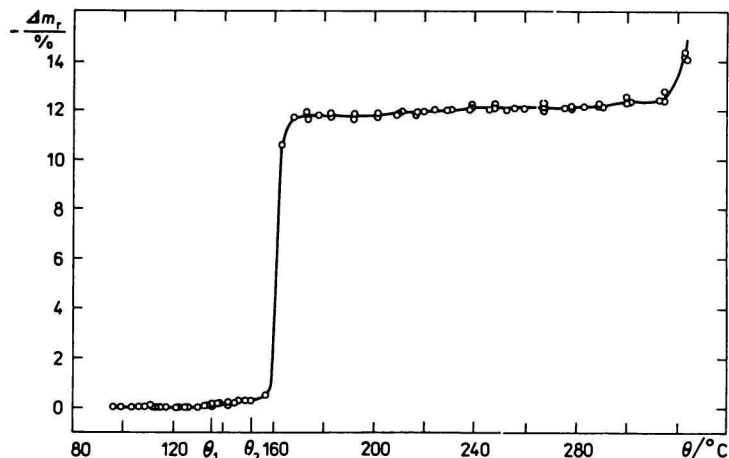
Fig. 1. Dependence of relative losses of mass of CaC_2O_4 H_2O on temperature. The sample was dehydrated for 24 h, pressure of water vapour was kept constant at 7.6 kPa.

Typical experimental dehydration curve showing the dependence of relative mass losses of CaC_2O_4 H_2O on temperature is plotted in Fig. 1. Relative losses of mass were recorded after 24 h heating of samples at partial pressure of water vapour 7.6 kPa. The whole temperature interval was divided into three parts and in each part 2—3 independent measurements were carried out. From the dehydration curve it can be seen that at the temperatures lower than θ_1 there are no changes in mass of sample exceeding the error of experiment. In the temperature range θ_1—θ_2 there is a small decrease in mass, approximately 0.3 % from the total mass of the sample. Dehydration of the main part of water takes place at temperatures higher than θ_2.

In Figs. 2—4, plots of relative mass losses *vs.* temperature at dehydration and rehydration of CaC_2O_4 H_2O at partial pressure of water vapour 7.6 kPa, 22.9 kPa, and 85.2 kPa obtained after 5 h, 24 h, and 71 h, respectively, are presented. It can be seen that at longer periods of isothermal heating the dehydration and rehydration curves approach each other. As follows from

Fig. 3 at sufficiently long time of heating these curves merge. The equilibrium curves plotted in Figs. 2 and 4 as dashed lines were obtained by interpolation of dehydration and rehydration curves obtained after 5 h and 24 h of measurement. From the course of the equilibrium curves it follows that in the region of dehydration of main part of water the equilibrium composition of solid phase changes fluently in broad temperature range. Boundary compositions of solid phases are close to CaC_2O_4 H_2O and CaC_2O_4, respectively. Thus we deal here with a divariant equilibrium. Coexisting phases are the solid solution and water vapour. Equilibrium composition of the solid solution at given temperature and pressure of water vapour is determined unambiguously.

For revealing of the nature of divariant equilibrium and of the nature of solid solution the criterion proposed by *Soustelle et al.* [16] was used. This criterion enables to distinguish between two thermodynamic models described above according to the shape of the isotherms $\varepsilon(p)$. The symbol ε denotes the ratio of
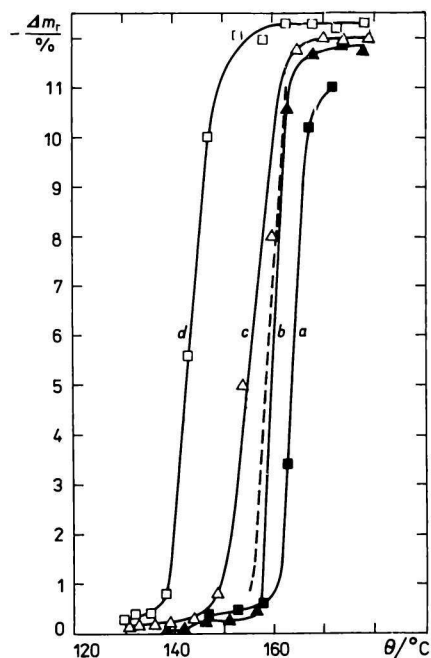

Fig. 2. Relative losses of mass of samples CaC_2O_4 H_2O as a function of temperature. Partial pressure of water vapour was 7.6 kPa. *a*) After 5 h dehydration; *b*) after 24 h dehydration; *c*) after total dehydration followed by 24 h rehydration; *d*) after total dehydration followed by 5 h rehydration.
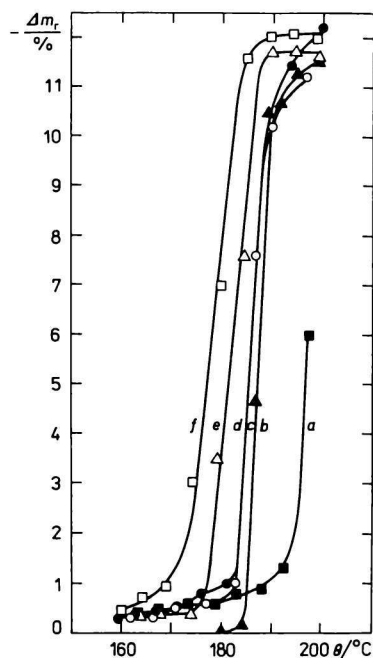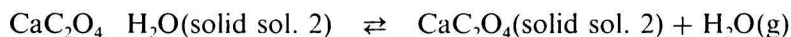
Fig. 3. The same as in Fig. 2. Partial pressure of water vapour was 22.9 kPa. *a*) After 5 h dehydration; *b*) after 24 h dehydration; *c*) after 71 h dehydration; *d*) after total dehydration followed by 71 h rehydration; *e*) the same as *d*) but for 24 h rehydration; *f*) the same as *d*) but for 5 h rehydration.

the amounts of substances of water and CaC_2O_4 in equilibrium solid phase. Adopting some simplifications the cited authors have shown that for the model of divariant equilibrium corresponding to the reaction scheme

$$CaC_2O_4(\text{solid sol. 1}) + H_2O(\text{solid sol. 1}) \quad \rightleftarrows \quad CaC_2O_4(\text{solid sol. 1}) + H_2O(g)$$
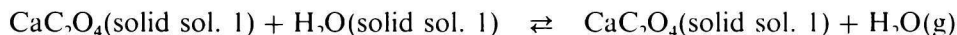
the function $\varepsilon(p)$ monotonously increases and when it is plotted the curve is concave with respect to the axis of positive values of ε. This model assumes the existence of solid solution of CaC_2O_4 and H_2O as an independent component.

The second thermodynamic model of divariant equilibrium is based on the reaction scheme

$$CaC_2O_4 \quad H_2O(\text{solid sol. 2}) \quad \rightleftarrows \quad CaC_2O_4(\text{solid sol. 2}) + H_2O(g)$$

Also in this case the function $\varepsilon(p)$ monotonously increases, however, its graphical plot is convex with respect to the axis ε. This model assumes the existence of substitution solid solution of CaC_2O_4 and CaC_2O_4 H_2O.
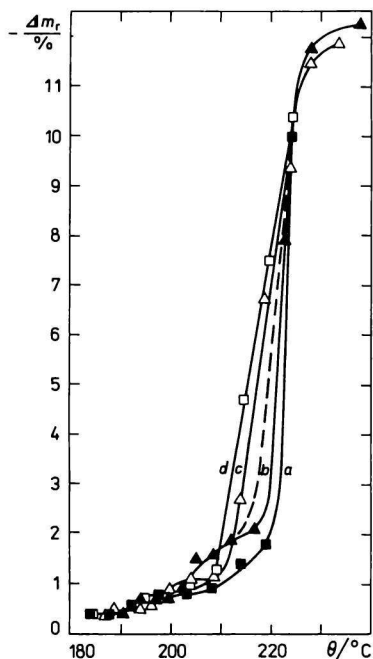

Fig. 4. The same as in Fig. 2. Partial pressure of water vapour was 85.2 kPa.

a) After 5 h dehydration; b) after 24 h dehydration; c) after total dehydration followed by 24 h rehydration; d) the same as c) but for 5 h rehydration.
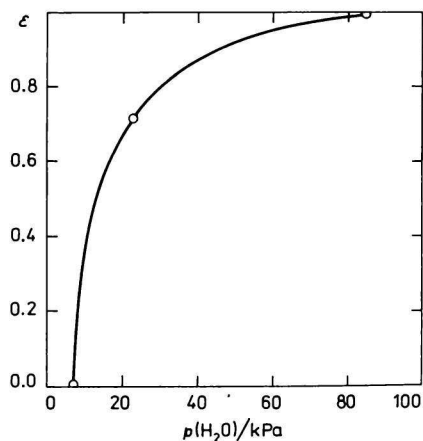
Fig. 5. Equilibrium composition of solid phase in the system CaC_2O_4 H_2O at the temperature of 185 °C as a function of pressure of water vapour. Composition of solid phase is represented by the parameter ε.

The values of $\varepsilon(p)$ were calculated for partial pressures of water vapour of 7.6 kPa, 22.9 kPa, and 85.2 kPa at the temperature 185 °C according to the relationship

$$\varepsilon = 1 - \frac{\Delta m_r}{100} \frac{M(CaC_2O_4 \ H_2O)}{M(H_2O)}$$

where $M(CaC_2O_4 \ H_2O)$ and $M(H_2O)$ are the corresponding molar masses. The obtained data are plotted in Fig. 5. The shape of this dependence corresponds to the second model, *i.e.* the solid solution of CaC_2O_4 and $CaC_2O_4 \ H_2O$ is formed. This conclusion is different from the opinion of *Gérard et al.* [13]. Dehydration mechanism proposed by these authors can induce the notion that solid solution of anhydride and water as an individual component is formed.
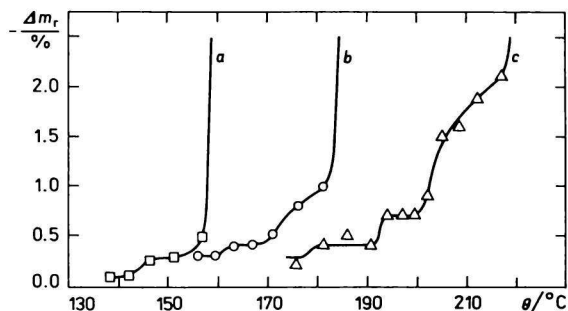

Fig. 6. Low-temperature parts of dependences representing the relative losses of mass of samples $CaC_2O_4 \ H_2O$ *vs.* temperature.
a) 24 h dehydration at the pressure of water vapour 7.6 kPa; *b*) 71 h dehydration at the pressure of water vapour 22.9 kPa; *c*) 24 h dehydration at the pressure of water vapour 85.2 kPa.

Special behaviour of the solid solution can be observed in the region close to the composition of $CaC_2O_4 \ H_2O$. In Fig. 6 the low-temperature parts of dehydration curves obtained for 24 h and 71 h at vapour pressures 7.6 kPa, 22.9 kPa, and 85.2 kPa are presented. At higher pressures of water vapour, when the temperature interval of main dehydration loss (temperature θ_2) is shifted to higher temperatures, the course of low-temperature part of the dehydration curves is more complicated. Dehydration in this temperature region proceeds through a series of divariant equilibrium states. Temperature intervals corresponding to these equilibrium states are narrow and composition of the solid phase remains constant in these intervals, *i.e.* no change in composition can be experimentally observed. Temperature regions corresponding to the constant composition of solid phase move with increasing pressure of water

vapour to higher temperatures. Similar shape of low-temperature parts of curves was observed at rehydration of CaC_2O_4. We assume that this phenomenon cannot be explained by gradual adsorption of water at the surface or in intercrystalline space of crystals CaC_2O_4 H_2O because the total loss of water never exceeded the stoichiometric amount of water in CaC_2O_4 H_2O. It seems also improbable that the amount of adsorbed water in CaC_2O_4 and in CaC_2O_4 H_2O was the same regardless of temperature and pressure of water vapours. Also in this case the total loss of water would not exceed the stoichiometric amount of water in CaC_2O_4 H_2O. The course of dehydration as it is shown in Fig. 6 can be explained by liberation of water molecules from their nonequivalent positions in the structure of solid solution. Relative distribution of water molecules bound in different types of nonequivalent positions in the
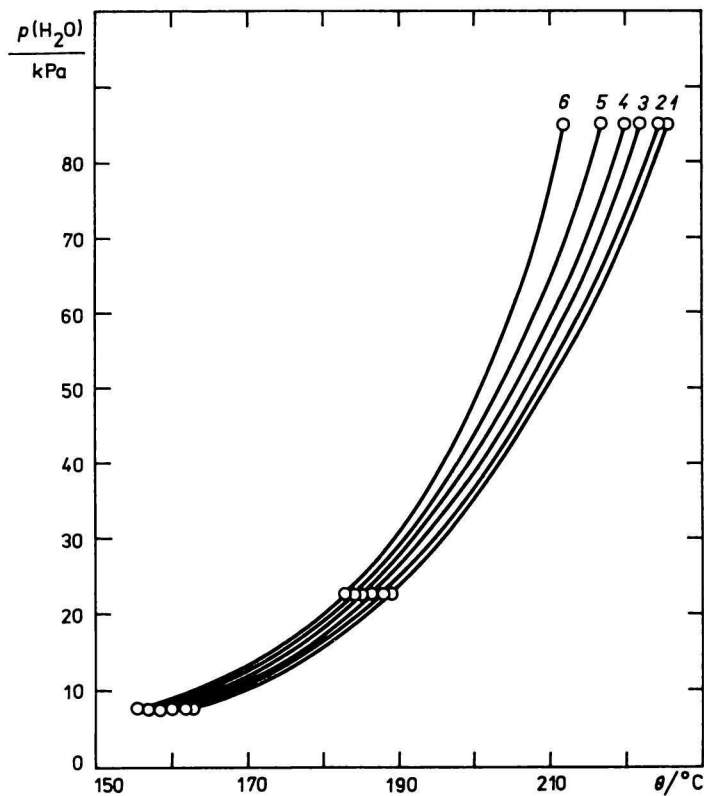

Fig. 7. Temperature dependence of equilibrium pressure of water vapour in the system CaC_2O_4—H_2O. Parameters of the curves are compositions of solid solution expressed as the ratio of amounts of substances of H_2O and CaC_2O_4 in the solid phase: 1. 0.11, 2. 0.19, 3. 0.35, 4. 0.51, 5. 0.68, 6. 0.84.

structure of solid solution depends on the pressure of water vapour which is in equilibrium with the solid solution.

Temperature dependences of equilibrium pressure of water vapour over solid solutions of different composition represented by the parameter $\varepsilon(p)$ are shown in Fig. 7. The equilibrium temperatures at corresponding pressures of water vapour obtained with the static method used in this work are about 5—15 °C lower than the values obtained by nonisothermal methods [13].

In the region in which the main part of water dehydrates the enthalpy of dehydration of solid solution can be determined from the slope of linear dependence $\ln [p_{rel}(H_2O)]$ *vs.* $1/T$ It was found that $\Delta H_{deh} = (69.8 \pm 3)$ kJ mol^{-1} This value is independent of composition and it is close to the value which was determined by *Gérard et al.* [13] and *Shimizu* and *Taniguchi* [14] for dehydration of CaC_2O_4 H_2O under the assumption of monovariant equilibrium.

References

1. Nerád, I. and Proks, I., *Chem. Papers 41*, 3 (1987).
2. Nerád, I., Vitková, S., and Proks, I., *J. Therm. Anal. 33*, 291 (1988).
3. Hoffmann, W *Naturwissenschaften 47*, 38 (1960).
4. Arnott, H. J., Pautard, F. G. E., and Steinfink, H., *Nature 208*, 1197 (1965).
5. Carmona, P., *Spectrosc. Lett. 8*, 645 (1977).
6. Shippey, T. A., *J. Mol. Struct. 63*, 157 (1980).
7. Tazzoli, V and Domeneghetti, Ch., *Am. Mineral. 65*, 327 (1980).
8. Deganello, S., *Z. Kristallogr. 152*, 247 (1980).
9. Deganello, S., *Acta Crystallogr., B 37*, 826 (1981).
10. Duval, D. and Condrate, R. A., Sr., *Phys. Status Solidi (b) 132*, 83 (1985).
11. Hocart, R., Gérard, N., and Watelle-Marion, G., *C. R. Acad. Sci. Paris 258*, Gr. 8, 3709 (1964).
12. Gérard, N. and Watelle-Marion, G., *C. R. Acad. Sci. Paris 261*, Gr. 8, 2363 (1965).
13. Gérard, N., Watelle-Marion, G., and Thrierr-Sorel, A., *Bull. Soc. Chim. Fr. 1968*, 4367.
14. Shimizu, S. and Taniguchi, M., *Nippon Kagaku Kaishi 7*, 953 (1977).
15. Soustelle, M., Gardet, J. J., and Guilhot, B., *C. R. Acad. Sci. Paris 270*, 212 (Ser. C) (1970).
16. Soustelle, M., Guilhot, B., Gardet, J. J., Watelle-Marion, G., and Mutin, J. C., *Bull. Soc. Chim. Fr. 1972*, 4509.