

KINETICS OF THE THERMAL DEHYDRATION
OF VARISCITE AND SPECIFIC SURFACE AREA
OF THE SOLID DECOMPOSITION PRODUCTS

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The surface properties of active solids resulting from decomposition of $\text{AlPO}_4 \cdot 2 \text{H}_2\text{O}$ by thermal treatment in vacuum and in air are studied in connection with the parameter governing the kinetics of the dehydration process. The values obtained for the activation energies of decomposition under isothermal conditions agree acceptably well with those computed from TG curves by the Freeman and Carroll method. Kinetic results, which are analysed in terms of the Mampel theory, strongly suggest that the activation energy of the nucleation process determines the rate of surface formation, and justify the observed fact that the specific surface areas of samples treated in vacuum are higher than those of samples treated in air.

The loss of constitutional or crystallization water of a solid during thermal treatment generally produces an increase of its surface area due to the breaking of the crystallites because of the internal vapour pressure [1–12].

Quantitatively, the increase of surface area is determined by the number of particles formed from each crystallite of the original phase, and this depends in turn on the relative values of the rates of formation and growth of the nuclei, which are the points from which the interphase originates [5, 8].

If the rate of formation of nuclei is high (free energy of activation small) compared to that of the growth of nuclei, each crystallite decomposes in a certain number of micelles, with the corresponding increase of the surface area. Conversely, if the rate of growth of the nuclei is high (small free energy of activation) each particle of the parent substance decomposes as a whole giving rise to a single micelle of the dehydrated product, and consequently the surface area will not increase sensibly with the fraction α of the original substance decomposed.

We report in this paper a study of the kinetics of the thermal dehydration of a synthetic orthorhombic aluminium phosphate dihydrate, found in nature as the mineral variscite, with the aim of obtaining information on the role of the activation energy of the nucleation process in the mechanism of surface area formation of the treated material.

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Materials and methods

Aluminium phosphate dihydrate was prepared according to a method described elsewhere [1]. The fresh material was allowed to dry under vacuum in a desiccator over CaCl_2 for several weeks; this gave a powdered product which was ground and sieved, the portion with particle size less than 80 microns being used in this study.

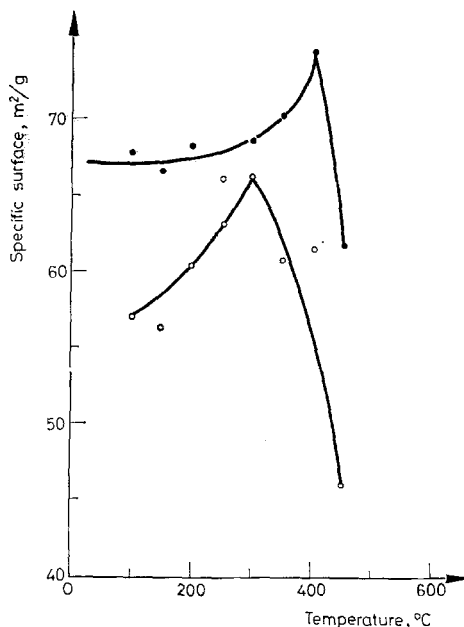


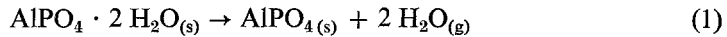
Fig. 1. Effect of temperature of thermal treatment of $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ on surface area of dehydrated products; ● in vacuum, ○ in air

Individual samples were activated in an electric furnace at 50, 100, 150, 200, 250, 300, 350, 400 and 450°, both in air and in vacuum, for a cumulative period of 5 hrs, and the surface area was determined by the B.E.T. method using nitrogen as adsorbate at -196° in a volumetric apparatus. The samples were previously gassed-out at 50° for 2 hrs. In the calculation of the results allowance was made for the deviation of nitrogen from the perfect gas laws. Some of the values obtained for the specific surface area of aluminium phosphate samples are given in Fig. 1 against the temperature of calcination.

TG and DTA curves were obtained in vacuum and in air by means of a Delta-therm D. 2000 apparatus. Another series of experiments was carried out at constant temperature in order to obtain the isothermal decomposition curves of the material. In every case, the substance used for the thermal measurements was always the fresh product.

Results and discussion

The characterization of the decomposition products of $\text{AlPO}_4 \cdot 2 \text{H}_2\text{O}$ suggests that this process can be represented by:



which under the employed experimental conditions can be considered irreversible [1].

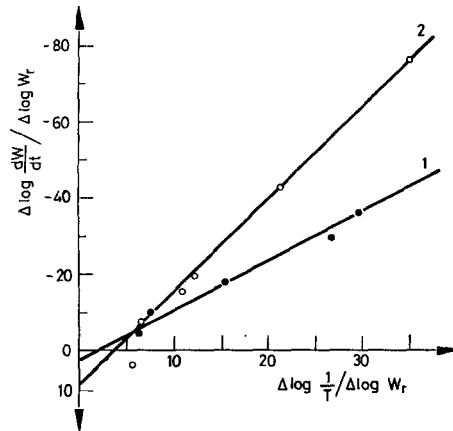


Fig. 2. Plot of weight loss vs. temperature for the thermal dehydration of $\text{AlPO}_4 \cdot 2 \text{H}_2\text{O}$ represented according to Eq. (2): curve 1, in vacuum; curve 2, in air

An estimation of the activation energy of the thermal decomposition of a solid at increasing temperatures, i.e. under the conditions of a TG experiment, can be obtained by the method of Freeman and Carroll [13] by means of an equation of the type:

$$\frac{E^*}{2.30 R} \frac{\Delta(1/T)}{\Delta \log W_r} = -n + \frac{\Delta \log \left(\frac{dw}{dt} \right)}{\Delta \log W_r} \quad (2)$$

where:

E^* = activation energy

n = order of reaction with respect to w

t = time

T = temperature ($^{\circ}\text{K}$)

R = gas constant

$\frac{dw}{dt}$ = rate of weight loss

W_c = weight loss at the completion of the reaction

W = weight loss at time t

$W_1 = W_c - W$ = weight of volatile substance remaining at time t .

In Fig. 2 the experimental weight loss is plotted according to Eq. (2). It can be seen that the experimental points fit two straight lines from the slopes of which the activation energy can be computed as 5.9 and 10.9 kcal/mole in vacuum and at atmospheric pressure, respectively.

However, because of the assumptions made in the derivation of Eq. (2), no confidence can be given to the actual figures and the only conclusion that can be drawn from it is that the activation energy corresponding to the process represented by Eq. (1) is much lower in the case of the decomposition in vacuum [14].

In an attempt to obtain more insight into the mechanism of the reaction, the thermal decomposition of aluminium orthophosphate dihydrate was also followed isothermally, both in vacuum and in air, at several temperatures between 100 and 300°. In Fig. 3 the values obtained for the fractional decomposition α are plotted versus time t , α being given by:

$$\alpha = \gamma(1 - W_t/W_0)$$

where W_t = weight of sample at time t ; W_0 = initial weight and $\gamma = \left(1 - \frac{v_b M_b}{v_d M_a}\right)^{-1}$ a constant depending on the molecular weights of the reactant and product solid phases and on the stoichiometry of the chemical reaction [15].

The shapes of the curves of Fig. 3 indicate the absence of both the induction and the acceleration periods characteristic of many isothermal decompositions, and show that the reaction is not complete in the range of temperature studied [16]. On the other hand, α varies linearly with t in the first minutes of the reaction, and then becomes more or less constant at a value which depends on the temperature at which the reaction is carried out and which in all the curves is too far removed from the maximum value of the decomposition, i.e. $\alpha = 1$, for being considered as a mere retention process; retention usually comprises only 2–3% of the decomposition [17].

These facts suggest that the nucleation process is dominant in determining the kinetics of the dehydration, as is frequently found in the case of very finely divided powders. The decomposition of each individual crystal results then from the formation of nuclei at its surface, and since the probability of nucleation can be supposed to be the same for every crystal, the rate of decomposition obeys a first-order kinetic law:

$$\log(1 - \alpha) = -kt + \text{const.} \quad (3)$$

This seems to be the case when aluminium phosphate dihydrate is decomposed at constant temperature, and this idea is supported by the curves of Fig. 4, which were obtained by plotting the experimental values of the fractional decomposition α versus time according to Eq. (3). It can be seen that during the first minutes of the reaction the data fit straight lines, the fit being the better the higher the temperature.

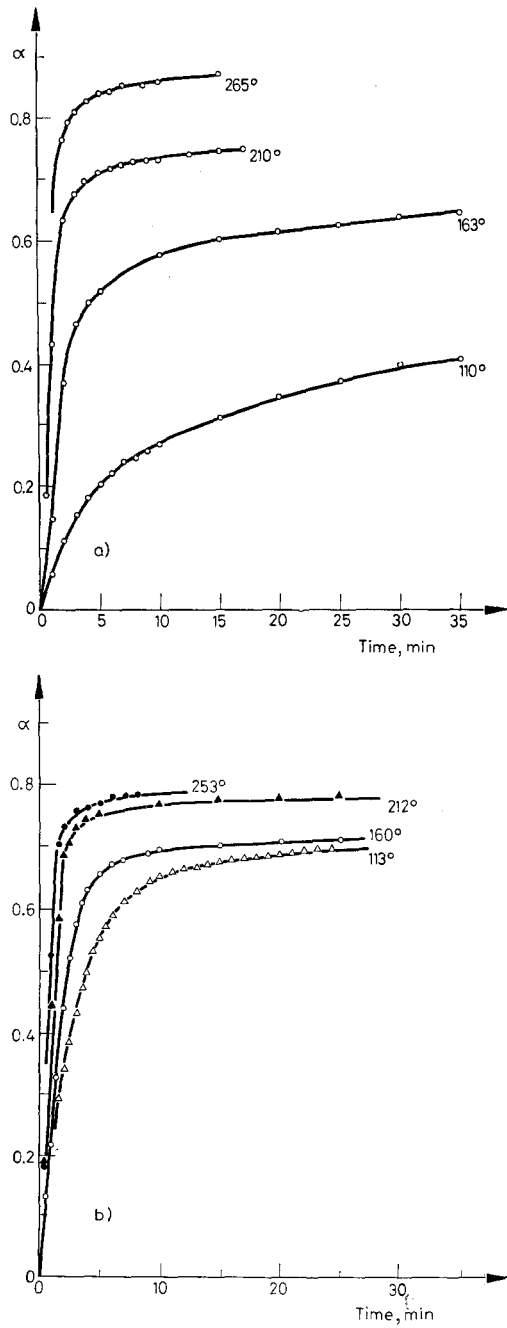


Fig. 3. Variation of the fractional decomposition α vs. time for the isothermal dehydration of $\text{AlPO}_4 \cdot 2 \text{H}_2\text{O}$: a) in air; b) in vacuum

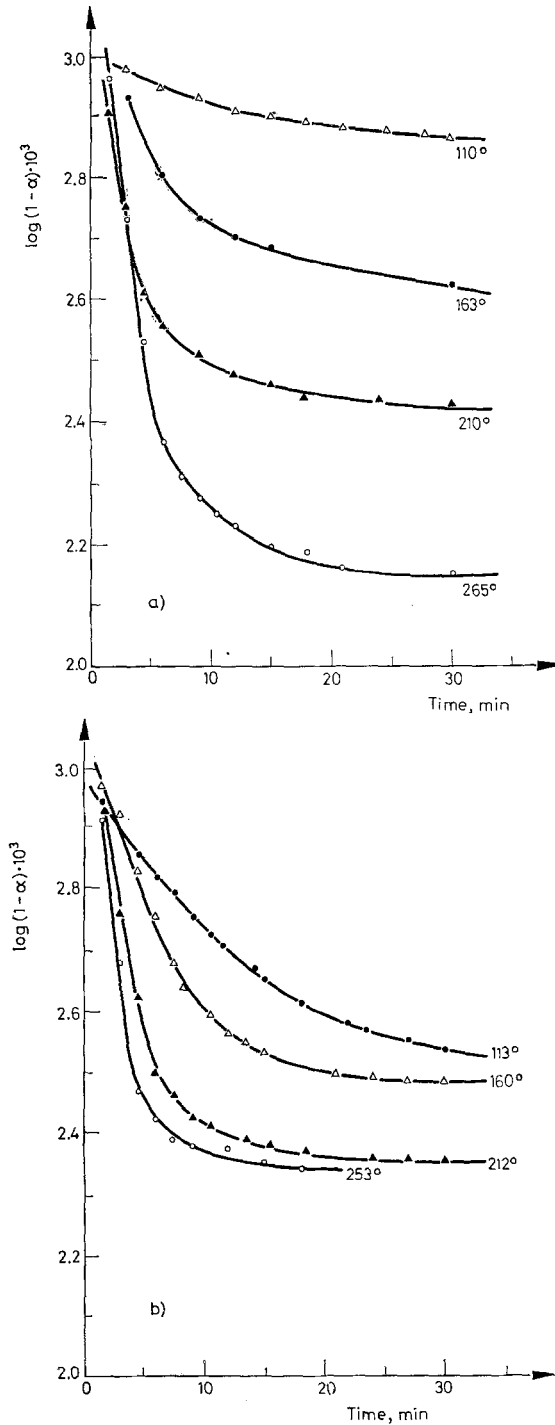


Fig. 4. Plot of $\log(1 - \alpha)$ vs. time for the isothermal dehydration of $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$:
 a) at atmospheric pressure; b) in vacuum

Interpretation of k

In his classical and comprehensive theoretical treatment of the thermal decomposition of powdered solids, Mampel [18] has shown that when the ratio between the radius of the particles, R , and the velocity of growth of the nuclei, k_2 , is small, the kinetics of the decomposition reaction should obey a unimolecular law, analogous to Eq. (3) with

$$k = 4\pi k_1 N_0 R^2 \quad (4)$$

and

$$t = t' - t_0 \quad (5)$$

where:

- k_1 = nucleation rate constant
- N_0 = number of potential nuclei forming sites per unit surface area
- t' = measured time
- t_0 = zero time evaluated from the experimental data
- t = corrected time.

The assumption made in this case is that the rate-determining step is the nucleation process and every particle is entirely consumed by the reaction which spreads out

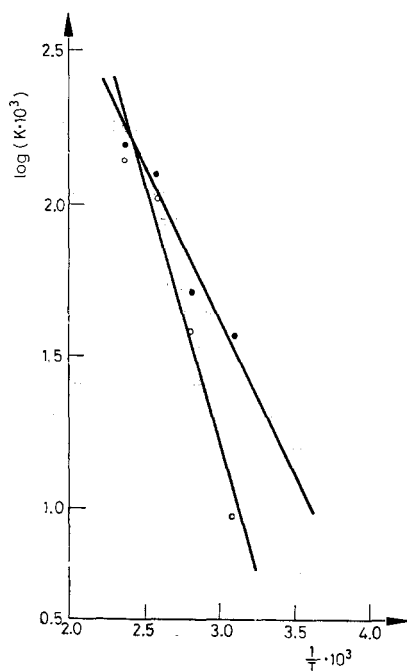


Fig. 5. Activation energies for the isothermal decomposition of $\text{AlPO}_4 \cdot 2 \text{H}_2\text{O}$. Plot of $\log k$ vs. T^{-1} for the dehydration in vacuum (curve ●), and at atmospheric pressure (curve ○)

from a single nucleus before the formation of any other nucleus takes place on its surface.

From the slope of the linear portions of the curves in Fig. 4 the activation energy of the decomposition process, E , can be obtained with the aid of an Arrhenius-type relationship. This is shown in Fig. 5, from which the values of 4.6 and 7.8 kcal/mole were obtained for E in the processes carried out in vacuum and in air, respectively.

According to Eq. (4), to obtain k_1 from k , and consequently the activation energy of the nucleation process, E , from the Arrhenius plot, it is necessary to know N_0 and R . Unfortunately, N_0 depends on the thermal history of the sample and changes with its thermal treatment. However, in the present case, it can be reasonably assumed that as the samples treated in air and in vacuum were analogous, N_0 and R are the same in both cases, and it is then possible to calculate the ratio of k_1 as a function of the activation energies. Thus,

$$\frac{k_{1,v}}{k_{1,a}} = \exp(E_a - E_v)/RT \quad (6)$$

where the subscripts v and a refer to the samples treated in vacuum and in air, respectively.

At 400°, this ratio is equal to approximately 11.

Nucleation rate constant and specific surface area

The above results indicate that the activation energy of nucleation is higher when the dehydration of $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ is carried out in air than when it is performed in vacuum. On the other hand, the values of the B.E.T. areas of the samples treated in vacuum are higher than those obtained when the sample is treated at atmospheric pressure. These facts seem not to be fortuitous but closely related, and in fact if the sample is formed by particles of the same size the average number of nuclei originating on the surface of each particle may be assumed to be proportional to the nucleation rate constant. On the assumption that every particle of the hydrated product decomposes to as many particles of about the same size and shape as nuclei are formed on their surface, it is easy to arrive at an expression which relates the ratio of nucleation rate constants with the specific surface areas of the decomposition products [19]:

$$\frac{S_a}{S_v} = \left(\frac{\rho_v}{\rho_a} \frac{\sigma_{3v}}{\sigma_{3a}} \right)^{2/3} \cdot \left(\frac{\sigma_{2,a}}{\sigma_{2,v}} \right) \cdot \left(\frac{M_v}{M_a} \right)^{1/3} \cdot \left(\frac{n_a}{n_v} \right)^{1/3} \quad (7)$$

where:

- S = B.E.T. areas of the treated samples
- σ_2, σ_3 = bi- and tri-dimensional shape factors
- M = formula weights of the dehydrated products
- n = number of particles resulting from each crystal of the parent solid
- ρ = densities of the samples

and a and v have the same meaning as above. Letting $\sigma_v = \sigma_a$ and $M_a = M_v$, Eq. (7) becomes:

$$\frac{S_a}{S_v} = \left(\frac{\rho_v}{\rho_a} \right)^{2/3} \cdot \left(\frac{k_{1,a}}{k_{1,v}} \right)^{1/3} \quad (8)$$

since $n_a/\dot{n}_v = k_{1,a}/k_{1,v}$.

For the sample treated at 400°, the following experimental values of densities and B.E.T. areas were obtained:

$$\rho_v = 1.75 \text{ g/cm}^3; \rho_a = 1.40 \text{ g/cm}^3; S_a = 61.5 \text{ m}^2/\text{g}; S_v = 75.5 \text{ m}^2/\text{g},$$

which substituted in Eq. (8) give a calculated value for the ratio S_a/S_v of 0.52. This compares reasonably well with the experimental value of 0.8 obtained from the ratio of the B.E.T. areas of the samples.

The preceding results emphasize the importance of the dehydration conditions of the parent product on the surface properties of aluminium phosphate, and suggest that the development of the surface area is strongly dependent on the activation energy of the nucleation process.

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RÉSUMÉ — On étudie les propriétés de surface des solides actifs provenant de la décomposition de $\text{AlPO}_4 \cdot 2 \text{H}_2\text{O}$ par traitement sous vide et dans l'air et on les rapporte aux paramètres gouvernant la cinétique du processus de déshydratation. Les valeurs obtenues en conditions isothermes pour les énergies d'activation de la décomposition sont en accord acceptable avec celles calculées à partir des courbes TG par la méthode de Freeman et Carroll. Les résultats

cinétiques qui sont analysés dans le sens de la théorie de Mampel font conclure que c'est l'énergie d'activation du processus de nucléation qui détermine la vitesse de la formation de la surface; ils justifient le fait observé que la surface spécifique des échantillons traités sous vide est plus grande que celle des échantillons traités dans l'air.

ZUSAMMENFASSUNG — Die Oberflächenbeschaffenheiten der aktiven Festkörper, welche bei der thermischen Behandlung im Vakuum oder in Luft als Zersetzungsprodukte von $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ entstehen, werden im Zusammenhang mit dem die Kinetik des Dehydratisierungsvorganges steuernden Parameter studiert. Die bei isothermen Bedingungen für die Aktivierungsenergien der Zersetzung erhaltenen Werte sind in befriedigender Übereinstimmung mit denjenigen, welche mittels der Methode von Freeman und Carroll aus den TG-Kurven errechnet wurden. Die gemäß der Mampel-Theorie analysierten kinetischen Ergebnisse lassen darauf schließen, daß die Aktivierungsenergie der Nukleationsvorgänge die Geschwindigkeit der Oberflächen-Entstehung bedingt und rechtfertigen die Beobachtung, nach welcher die spezifische Oberfläche vakuumbehandelter Proben größer ist als die der luftbehandelten.

Резюме — Изучены свойства поверхности активных твердых веществ, образующихся при термораспаде $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ в результате термической обработки в вакууме и в воздухе, в связи с параметром, направляющим кинетику процесса дегидратации. Величины, полученные для энергии активации распада при изотермических условиях, удовлетворительно совпадают с величинами, рассчитанными по кривым ТГ методом Фримена и Керролла. Полученные кинетические данные, проанализированные, исходя из теории Мампела, указывают, что энергия активации процесса образования ядер определяет скорость образования поверхности и подтверждают наблюдаемый факт, что удельная поверхность образцов, обработанных в вакууме, выше, чем в случае обработки в воздухе.