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Solid state decompositions

In celebration of the 60^{th} birthday of Dr. Andrew K. Galwey

KINETICS AND MECHANISM OF THE DEHYDRATION OF α-$NiSO_4 \cdot 6H_2O$

G. G. T. Guarini

Dipartimento di Chimica, Chimica Fisica delle Interfasi, Universita di Firenze,
Via G. Capponi, 9–50121 Firenze, Italia

Abstract

A study of the thermal dehydration of α-$NiSO_4 \cdot 6H_2O$ has been performed by power compensation differential scanning calorimetry in flowing nitrogen. No significant differences in behaviour were observed using either uncrushed crystalline powders or single crystal slabs cleaved parallel to {001}. In good agreement with previous findings, the kinetic analysis of the thermal curves confirms the validity of a $n = 2$ Avrami-Erofeev equation (AE2) in isothermal experiments at low (338–343 K) temperatures or in the initial portions of variable temperature runs. The kinetic obedience is however of an 'order of reaction' type for the main portion of the variable temperature runs and, for isothermal experiments, in the upper part of the temperature range investigated. Values of activation energies and frequency factors are reported.

Parallel studies by optical microscopy showed relevant changes of surface texture when partially (thermally or vacuum) dehydrated {001} cleaved surface were submitted to rehydration. This phenomenon (named orange peel formation) indicates that a dehydrated layer forms on the crystal surfaces preceding the appearance of product crystals (germination or nucleation). Microscopy also revealed that reaction goes on inside the crystal and that product formation takes place in the bulk phase, following lattice collapse in experiments at high heating rates.

Combined with previous results, these new experimental findings allow us to formulate a mechanism for the present transformation, comprising three main rate processes:

i) the reaction (detachment of water molecules from their lattice positions in the reactant);

ii) the migration of the water molecules freed by the reaction through the initially formed, water-depleted layer enveloping the reactant crystal;

iii) the crystallization of such a layer to form the product.

Keywords: α-$NiSO_4 \cdot 6H_2O$, dehydration, kinetics

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Introduction

Tetragonal nickel sulphate hexahydrate has received considerable attention by researchers studying the dehydration reactions of crystal hydrates. The formation in vacuum of a probably amorphous dehydrated phase was reported by Frost [1–3], who also determined the excess energy stored therein, in agreement with Fricke's observations [4]. A detailed kinetic study of the vacuum dehydration of the same salt, particularly devoted to the problem of enhanced reactivity at defects, was performed by Thomas and Renshaw [5–6], who reported the kinetic obedience of the decomposition to the AE2 law and a partial (up to 50%) correspondence of the nucleation sites with the sites of emergence of dislocation lines, as revealed by the etching technique. From synchrothron radiation studies, Sheen and Sherwood [7, 8] found, however, that etch pits could also be formed on the surfaces of crystals devoid of dislocations. Recent evidence about the existence of two kinds of pits [9], reconciled this apparent disagreement. The peculiar properties of the nickel salt, which emerged from previous reports [1–8], prompted us to undertake a preliminary study of this decomposition by heat-flux thermal analysis and optical microscopy. Some special aspects of this dehydration, like lattice collapse and bubble formation [10], or dependence on heating rate (σ in deg·min^{-1}) [11] emerged. Such findings could be interpreted by postulating the initial formation of a dehydrated layer on the surfaces of the crystals. This layer was later proved to exist by means of the photoacoustic technique [12].

Aiming to ascertain the role played by such a layer in the kinetics and mechanism of the transformation, the present study complements the previous findings with data from the power compensation thermal technique, which is reputed to be more reliable for the determination of kinetic parameters [13]. Further information was obtained by optical microscopic studies of freshly cleaved {001} surfaces, submitted either to dehydration-rehydration cycles inside the 'ad hoc' cell of the microscope, or to rapid temperature increases in the cell of a thermal apparatus.

Experimental

Large (up to cm size) single crystals of α-$NiSO_4 \cdot 6H_2O$ of good perfection were obtained as previously described [11]. Cleavage parallel to {001} was performed by a sharp blow with a suitably oriented razor blade. Crystalline powders were precipitated, from the same saturated solutions used for single crystals preparation, by sudden addition of acetone. After separation, these powders were 'dried' at room temperature under reduced pressure. Microscopic examination indicated that powders consisted mainly of truncated bipiramids of ca. 0.03 mm mean size; rare square plates of ca. 0.1 mm were also observed.

15–25 mg samples of either powders or doubly cleaved {001} single crystal slabs were weighed in the standard aluminium sample pans of a Perkin-Elmer DSC7 Differential Scanning Calorimeter used in either isothermal or non-isothermal mode. To test the role of surface perfection, some experiments were performed using cleaved crystals whose surfaces had been fully scratched by gently rubbing with emery paper. As a rule, lids were used to loosely cover both reference and sample pans in order to match thermal emissivity. The calorimeter cell was always flushed with dry nitrogen flowing at 16 $\mathrm{ml \cdot min^{-1}}$. In isothermal experiments, the flow of the purge gas was started only after equilibration of the apparatus at the temperature of the experiment. Isothermal decompositions were performed in the temperature range 338–363 K. In some experiments in the upper part of the range investigated (358–363 K), the stabilization period of the apparatus overlapped with the beginning of the transformation; these runs were discarded. In non-isothermal experiments, previous experience [11], suggested that the heating rate, σ, should be kept in the 0.1–2 range; higher σ values were seldom used and only for comparison with previous findings by the heat-flux apparatus. At the end of every experiment, mass loss determinations allowed the calculation of the extents of dehydration reached.

Kinetic analysis of the isothermal curves was performed on percent decomposition (α), and time (t) data to compare the fits of the commonly used rate equations [14] over the whole range of α, or parts of it. Non-isothermal curves were analysed by means of the Perkin-Elmer software; or α and $d\alpha/dT$ were evaluated at several temperatures and the differential method of Sharp and Wentworth [15], was used.

A Reichert Zetopan optical microscope, equipped with interference contrast and with an Olympus OM2 camera, was used in the reflection mode to reveal the texture changes taking place on freshly cleaved {001} crystal surfaces when, after partial dehydration in dry nitrogen or vacuum, they were allowed to rehydrate in wet nitrogen or in the laboratory atmosphere. In these experiments, a cell already described [16] was used and evacuation to ca. 10^{-2} Pa was ensured by an oil diffusion pump. Product formation in the bulk phase was tested by means of the previously used assemblage of a Perkin-Elmer DSC 1b Differential Scanning Calorimeter and a Wild M5A reflection microscope [10].

Results

Some typical isothermal runs in the temperature range 338 K$<T<$363 K are shown in Fig. 1. In these experiments, the amount of water lost increases somewhat with temperature, going from 3.8 water molecules at 338 K to 4.2 at 363 K. The heat of dehydration per mole of water, evaluated from these curves, remains fairly constant at 54±2.5 kJ·mol^{-1}, in good agreement with previously reported data [11]. In most of the experiments in the low temperature range, the separation between surface and bulk dehydrations [11] was observed again, Fig. 2, and tested with blank experiments; heat evaluations confirmed that the surface portion of the dehydration amounts to a few percent of the total heat of dehydration [17]. Considering that in these temperature conditions the sample loses ca. 4 of the six water molecules, a rough calculation, based on equal loss from all the surfaces of a cube of the same mass as the sample, allows us to deduce that the thickness of the dehydrated outer layer is of the order of a few μm.

The kinetic analysis of the isothermal runs revealed perfect agreement with AE2 covering the complete range of α, particularly at low temperatures. The kinetic parameters, (Fig. 3), were evaluated as $E_a = 86.2\pm7.5$ kJ·mol^{-1} and $\ln(A/\text{min}^{-1}) = 24.4\pm2.2$, in good agreement with previous findings [6]. In the upper part of the temperature interval, the α range of obedience to AE2 narrows

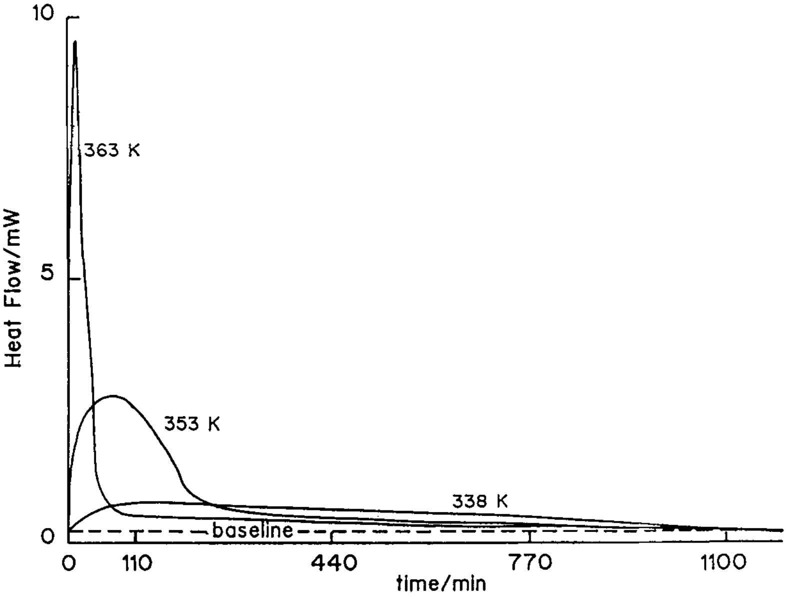

Fig. 1 Characteristic change in shape of the isothermal DSC curves with the temperature

progressively. The best fit over the complete α range changes to 'order of reaction' type equations; correspondingly the activation energy doubles (first-order equation).

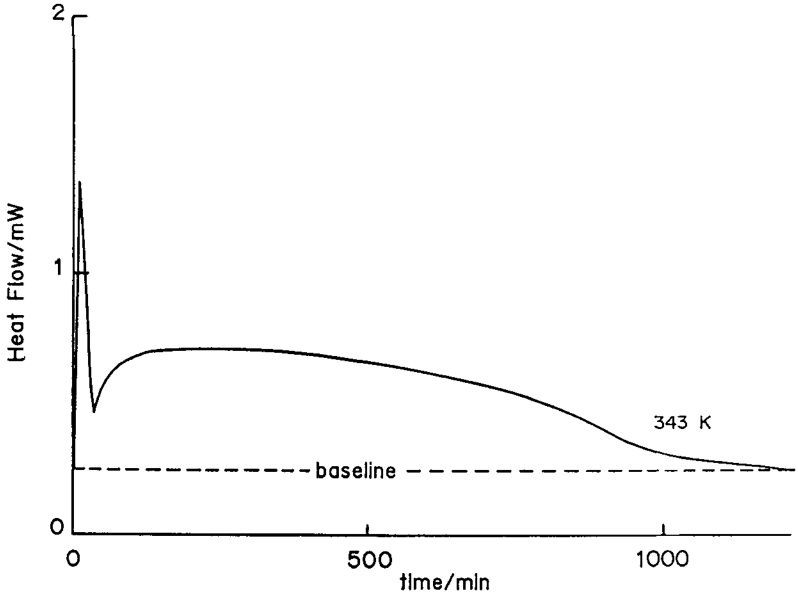

Fig. 2 Separation of interphasal (initial peak) and bulk (main curve) dehydrations that can be achieved in low *T* runs

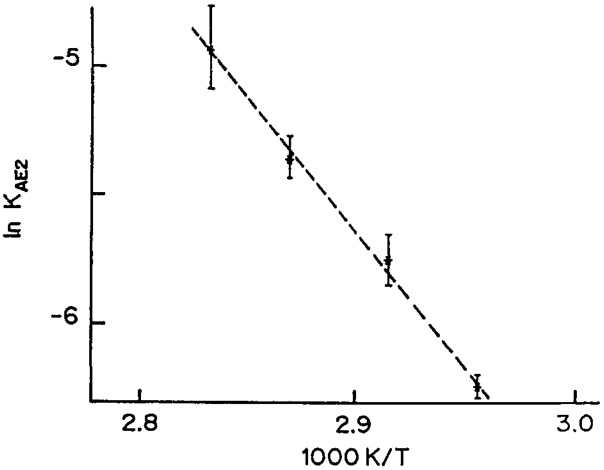

Fig. 3 Arrhenius plot for the isothermal runs in the low *T* range (AE2 fitting)

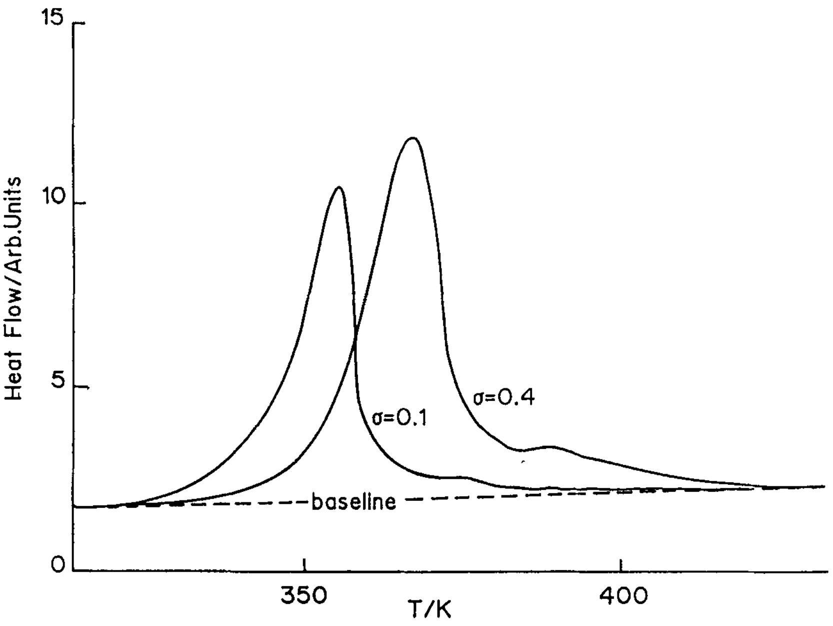

Fig. 4 Typical DSC curves recorded at different σ. As well as shifting the curves towards higher temperatures, the increase in σ enhances the importance of the shoulder at high T attributed to water retention. (For illustrative purposes the ordinates have been adjusted)

The heat of transformation per mole of water, deduced from increasing temperature runs (53.1±3 kJ·mol^{-1}), almost exactly matches the value found previously [11]. Two typical thermograms, in which five of the six water molecules are lost [6], are shown in Fig. 4. Kinetic analysis shows that, even at the lowest values of σ, the AE2 equation fits the data only for an initial portion ($\alpha < 0.15$) of the decomposition. For this portion of the reaction, the values of activation energy and preexponential factor {$E_a = 76.1 \pm 14.6$ kJ·mol^{-1}, $\ln(A/\text{min}^{-1}) = 21.9 \pm 4.8$} compare with those deduced from isothermal experiments. Best fit for the overall dehydration is however given by an 'order of reaction' equation. The mean value of reaction order n, from over 30 experiments at various σ, is 2.03 ± 0.6. Plots of $\ln[1/f(\alpha)\cdot d\alpha/dT]$ *vs.* $1/T$, when $f(\alpha)$ is the second-order equation, are either perfectly linear (Fig. 5(a)), or show oscillations along the regression line (Fig. 5(b)). There is some indication that the linearity improves in the upper part of the σ range. From both kinds of plots (or from the corresponding analysis by the Perkin-Elmer software) very high values for ac-

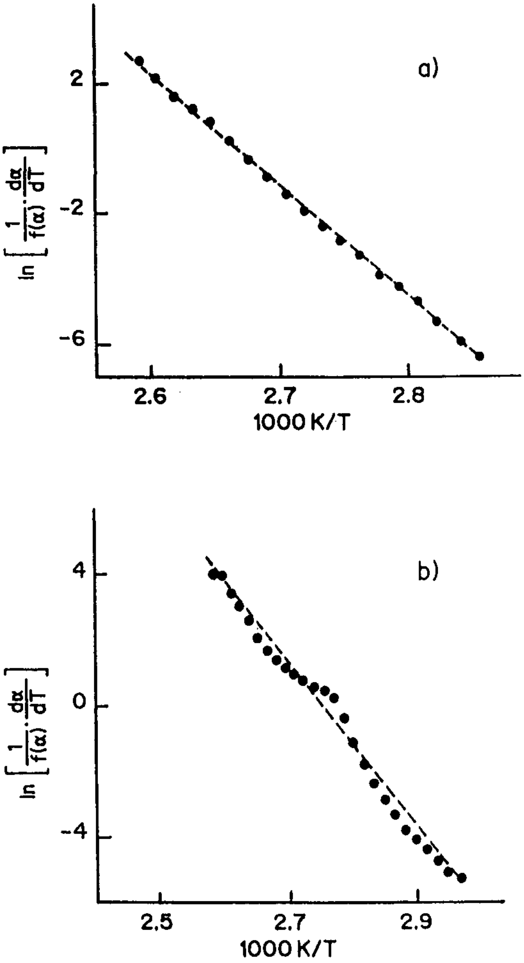

Fig. 5 Perfectly linear (a) or oscillating (b) Arrhenius plots obtained using the second-order equation as $f(\alpha)$. The two experiments were chosen on the extremes of the E_a variance

tivation energy (251±27 kJ·mol^{-1}) and frequency factor {ln(A/min^{-1}) = 76.2±9.2} were deduced.

In good agreement with previous findings for crushed powders [11], when crystals with the surfaces scratched were used in experiments with $\sigma<0.4$, the range of α in which the AE2 equation is applicable expands ($0.01<\alpha<0.80$). The activation parameters evaluated from these runs are E_a = 70.7±7.9 kJ·mol^{-1} and ln(A/min^{-1}) = 22.2±2.4.

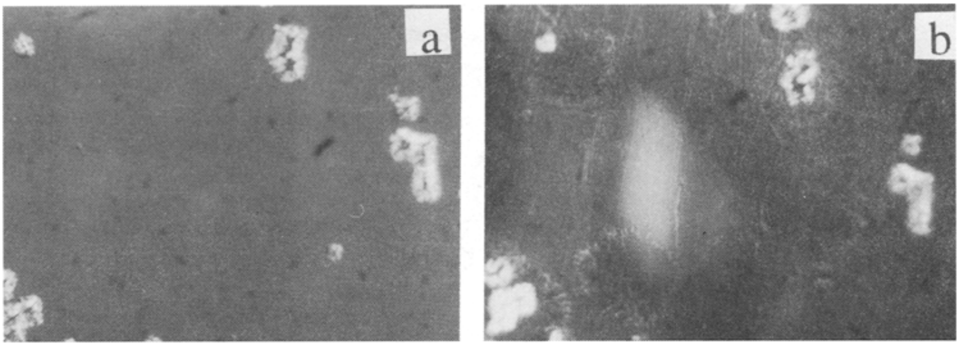

Fig. 6(a) {001} cleavage surface dehydrated in vacuum up to the formation of some 'nuclei' at random positions; (b) the same surface after exposure to wet nitrogen: as well as some rehydration of the nuclei, the texture change of the unaltered surface (orange peel formation), which is proof of general rehydration, is evident. (× 85)

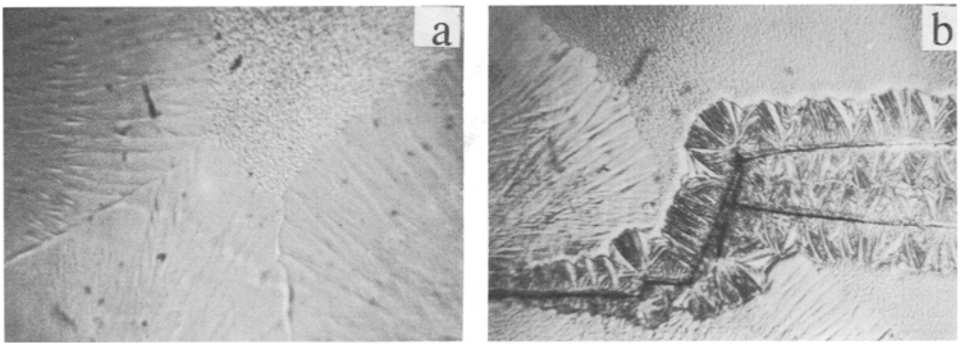

Fig. 7 Peculiar retexturing of different parts of a cleavage {001} surface, taken to the laboratory atmosphere after partial (insufficient to reach 'nucleation') dehydration. The crystal comes from a low temperature isothermal run interrupted while the initial (interphasal) peak was ending. The retexturing is particularly dramatic at cleavage surface steps. (× 210)

Microscopic observation of the rehydration behaviour of partially vacuum-dehydrated {001} cleavage surfaces gave the expected results. In Fig. 6(a) a freshly cleaved surface is photographed inside the evacuated cell. Some small dehydration 'nuclei' are observed, while the remaining surface is perfectly flat. The texture change (orange peel formation) of the same surface, after rehydration by admission of wet N_2, is shown in Fig. 6(b). On the other hand, Fig. 7 shows that the same happens to a surface whose dehydration was interrupted before the appearance of product aggregates. A sequence of micrographs taken during a dehydration experiment in the microscope cell is shown in Fig. 8.

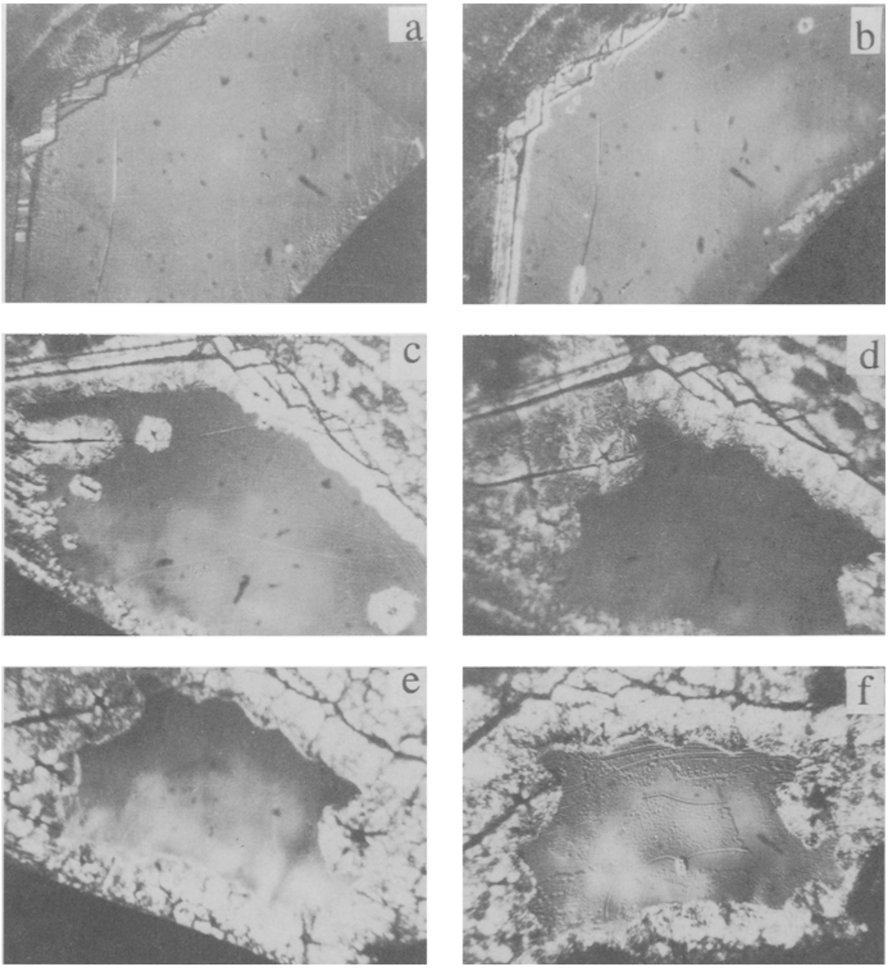

Fig. 8 Formation of 'orange peel', (f), on a zone of the surface of such perfection as to prevent product crystallization (nucleus formation) until the vacuum dehydration is almost complete.(× 85)

When, at the end of the experiment, air is admitted into the cell the 'orange peel' forms on the portion of the surface devoid of growing product patches.

The typical result of some experiment with cleaved single crystals, heated at $\sigma>8$ in the Perkin-Elmer DSC 1b apparatus and simultaneously observed and photographed with the Wild microscope, is shown in Fig. 9. After the previously described [10] lattice collapse, shown by cracking, the formation of tiny particles of the monohydrate product is clearly evident on cracks below the surface. This is taken as definite proof that the reaction goes on in the bulk phase, after the initial formation of a dehydrated layer on the crystal surface. While cracking and inner nucleation take place, no significative growth of the product 'nuclei' on the surface is observed.

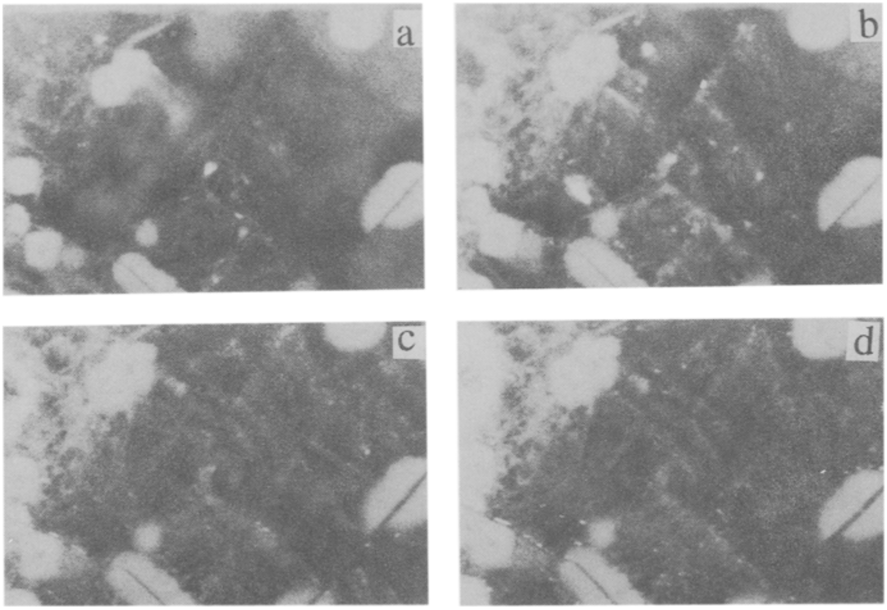

Fig. 9 Inner lattice collapse (cracking) of a crystal heated at high (>8) σ. The phenomenon, already begun in (a), expands in (b) and (c), while tiny particles of monohydrate (yellowish in the original colour frames) decorate the array of cracks. Surface product patches (large white) do not grow while the inner process takes place, (b), (c), (d). (×35)

Discussion

Obedience to the Avrami-Erofeev equation is often considered sufficient proof to identify the mechanism of a solid state reaction as a nucleation-and-growth one. In the present instance, the above might have been justified for low temperature isothermal decompositions, but the value observed for the exponent n (sum of the nucleation law, β, and of the dimensionality of the nucleus, λ, [14, 18]) is apt to arouse some suspicions. In fact the nucleation is not instantaneous ($\beta > 0$) and the nuclei are three-dimensional ($\lambda = 3$), so a value of at least

4 was expected for n in place of the observed 2. Furthermore, other previously described aspects of the dehydration behaviour of nickel sulphate hexahydrate have to be taken into consideration, namely:

i) the separation of surface and bulk dehydration endotherms;

ii) the typical behaviour of crystals when heated at relatively high σ (> 4);

iii) the photoacoustic response of partially dehydrated cleaved crystals and powders;

iv) the special etching behaviour of freshly cleaved surfaces.

Items (i–iv) strongly indicated that any interaction of the crystals with the exterior was dominated by the properties of the outer regions of the crystals. This is in contrast with the nucleation-and-growth theory commonly accepted as the basis for the interpretation of reactions of this kind [14, 18–21]. The present work, completing the information about the dehydrated surface layer by verifying the formation either of the 'orange peel' or of product in the bulk phase and evaluating thermal curves more reliable for kinetic interpretation, allows us to propose an interpretation of the dehydration of nickel sulphate hexahydrate crystals that is believed to account for the whole spread of experimental findings.

The formation of orange peel confirms that the first event of the dehydration of the crystals is the elimination of the gaseous product from a certain number of the outer lattice planes, recently identified [9] as those modified by the presence of the surface. Such displacement of water molecules from their lattice positions in the reactant is here recognized as reaction. So the first result of reaction is the formation of a dehydrated surface layer (a process which appears in some experiments as a separate thermal event) that encloses the unchanged reactant in a continuous film, through which the water molecules generated by further reaction must find their way to the gas phase. As a consequence, the rate of migration of the water molecules through the dehydrated layer can become determining when such a surface films is poorly permeable (as in the present case). The formation in the dehydrated layer of the first crystalline germs of the product and their growth (processes here collectively named product crystallization) is the last step of the overall transformation and is probably the slowest. In fact, geometries conducive to the lattice arrangement of the product (as found at defective sites [22]) and the presence of water [23–25] are required. However, product crystallization introduces discontinuities in the initially formed layer and makes it permeable to the water molecules generated by the progress of the reaction in the bulk phase underneath. This may increase the reaction rate.

The observed dehydration behaviour of α-$NiSO_4 \cdot 6H_2O$ crystals is the result of the interplay of the above three steps. The variations of their relative importance during the transformation can account for the observed changes of kinetic obedience.

Isothermal runs

The fitting of isothermal runs by the AE2 equation, in the low part of the temperature range, might be interpreted as indicating a simple nucleation-and-growth process. However, as well as the unexpected value of n discussed above, evidence is found that the reaction takes place on the whole crystal surface rather than at the reactant/product interface, assumed to be at the nucleus boundary in the nucleation-and-growth theory. Furthermore, the fact that reaction has been proved to go on in the bulk, leading to lattice collapse and then to product crystallization on generated defects (crack edges), is another clear indication that the observed formal obedience to the AE2 equation needs some consideration.

When the temperature of the isothermal experiments is low, the rate of product crystallization compares with that of reaction, so that the continuity the initially formed dehydrated layer is disrupted by the formation of crystalline product. Channels are formed through which water can escape almost freely: the reaction goes to completion smoothly.

Product crystallization is an exothermic process and therefore is not favoured by temperature increases so, at higher temperatures, the crystallization process becomes insufficient to produce the necessary discontinuities in the surface layer and diffusion of water through it may control the overall transformation. This is supported by the observed decrease of n from 2 to 1 (the AE1 equation is equivalent to the first-order equation) that can also be interpreted as due to diffusional control [26] (see also [14], p. 68 ff.). Indirect support to the above is given by the AE2 obedience observed in the initial portions of the variable temperature runs. In fact, in all the experiments at $\sigma<1$ (i.e. in the greatest part of the present experiments), α reaches 0.15 at temperatures $\leq$ than those of the upper part of the isothermal range.

Another experimental result not considered up to now must be taken into due consideration. Previous experiments at $\sigma = 4$ showed that, at temperatures slightly higher than 373 K, a sort of superficial fluidification takes place and surface nuclei no longer grow, (Ref. [10], Figs 2 and 3). This is confirmed here, Fig. 9. The permeability of this fluid layer to water molecules must be extremely poor and further reaction leads to bubble formation [10]. The present experiments, isothermal (or non-isothermal, but at much lower σ values), make it plausible to believe that the surface layer becomes hardly permeable at lower temperatures (ca. 363 K). Coupled with the regression of the crystallization equilibrium, this leads to the diffusional control that may explain the first-order behaviour observed in the upper part of the temperature range of the isothermal runs.

Non-isothermal runs

When the temperature increases, the same crystallization problems and the enhancement of the rate of reaction cause the increase of the pressure of the volatile product in the bulk phase that is responsible for the extreme phenomena described above. These are not observed at the low σ values used here, nevertheless the very high value for the activation energy found for second-order decompositions indicates the presence of a relevant pressure of the gaseous product at the reaction site [27] and supports the present point of view.

There are two possibilities to account for the observed second-order obedience:

i) the high internal pressure reduces the reaction rate and, from a diffusion controlled first-order process, a second-order obedience originates. If we use the exponential form of the first order equation, $1/(1-\alpha) = \exp(kt)$, and assume kt small (i.e. k is very small for inner pressure effect), then $1/(1-\alpha) = 1+kt$ or $1/(1-\alpha)-1 = kt$ which is the second-order equation;

ii) two different mechanisms, one of low and one of high activation energy, operate concurrently simulating overall second-order obedience: these are the more-or-less 'damped' reaction and an unknown process, of very high activation energy, which succeeds in releasing the product pressure in the bulk phase. The latter process might be tentatively envisaged as any sort of heavily hindered migration of water molecules, either through the poorly permeable fluid phase, or through the limited number of channels present in the already crystallized product (which has stopped growing and whose channels probably become obstructed by the fluid phase). The experimental results appear to give support to both possibilities. Both strict linearity {item(i) see Fig. 5(a)) or oscillation along the regression line {item ii) see Fig. 5(b)} are found when the 'second-order' $f(\alpha)$ is used. It is believed that the final shape of the Arrhenius plots is mainly determined by properties that may change from crystal to crystal, like the degree of perfection etc. In any case, the observed tendency of the linearity to improve when σ increases is in agreement with the above interpretation. Other dehydrations (including that of nickel sulphate heptahydrate) showing the same kind of behaviour have been reported [28] and interpreted in a similar way.

The experiments conducted with cleaved crystals whose surfaces were deliberately scratched with emery paper give further support to the above interpretation. The mechanical damage of the exposed surfaces creates a large number of defective sites conducive for product crystallization and speeds up the rate of this process thus ensuring an easy escape for the product molecules. The reaction step remains rate determining up to relatively high σ value. The value of the activation energy determined from these experiments is the lowest observed and is believed to be the most reliable for the reaction.

Conclusions

Notwithstanding the appearance of beautiful nuclei on the surfaces of the crystals submitted to dehydration and the formal obedience to AE2 in low temperature experiments, the dehydration of α-$NiSO_4 \cdot 6H_2O$ cannot be considered a 'nucleation-and-growth' reaction. The mechanism of dehydration is a complex one and is dominated by the properties and behaviour of the outer parts of the crystal. The overall transformation can be interpreted in terms of three steps identifies as reaction, water migration and product crystallization, the last being the slowest.

When the temperature of the isothermal experiments is low, the rate of product crystallization is comparable with the rate of reaction and the relatively free escape of the gaseous product through the initially formed dehydrated surface layer is ensured by the interparticle channels of the crystalline product. The same happens in the initial (low temperature) portions of the variable temperature runs, as well as in those experiments in which crystal surfaces have been damaged by scratching (or crushing, if powders are considered) which greatly enhances the number of surface defects and hence the rate of product crystallization. It is from the latter kind of experiments that the best value for the activation energy of the reaction is deduced.

When product crystallization cannot ensure the free escape of the reaction product, water migration (diffusion) becomes rate determining and the kinetics switches to first-order behaviour (high temperature isothermal runs).

The reaction is found to continue in the bulk, even when the formation of an almost impermeable surface layer (observed in high σ runs) becomes responsible of the increase of bulk product pressure, leading to the second-order kinetics found for non-isothermal runs.

There are analogies between the present dehydration reaction and those of common and chrome alums [29]. This reinforces the opinion that the main characteristics of the present system (the initial formation of a dehydrated layer on the surfaces of the reactant crystal and the dependence of the progress of the transformation on its properties) will be found operative also in the dehydration of other materials. All crystal hydrates for which enhanced nucleation, orange peel formation or Smith-Topley effect (all phenomena indicative of surface-layer dependence) have been observed are expected to decompose according to the above scheme, with small variations due to factors specific to the crystal examined (e.g. surface perfection, permeability of the dehydrated layer etc.).

The present work also constitutes another proof that obedience to a certain kinetic equation cannot be used as evidence of mechanism.

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Zusammenfassung — Mittels DSC in strömendem Stickstoff wurde die thermische Dehydratation von -$NiSO_4 6H_2O$ untersucht. Zwischen dem Verhalten unzerkleinerter kristalliner Pulver oder einzelnen, parallel zu {001} gespaltenen Kristallplättchen konnte kein signifikanter Unterschied festgestellt werden. In guter Übereinstimmung mit vorangehenden Resultaten bestätigt die kinetische Analyse der thermischen Kurven in isothermen Versuchen bei niedrigen Temperaturen (338–343 K) oder in den Anlaufphasen von variablen Temperaturdurchläufen die Gültigkeit einer n=2 Avrami-Erofeev-Gleichung (AE2). Für den Hauptteil der variablen Temperaturdurchläufe unterliegt die Kinetik einer Reaktionsordnung und wurde für isotherme Experimente im oberen Teil des Temperaturbereiches untersucht. Werte für Aktivierungsenergien und Frequenzfaktoren werden beschrieben.

Parallel durchgeführte Lichtmikroskopieuntersuchungen zeigen deutliche Veränderungen der Oberflächentextur, wenn eine (thermisch oder durch Vakuum) partiell dehydratierte {001} gespaltene Oberflächen einer Rehydratation ausgesetzt werden. Diese Erscheinung (mit dem Namen Orangenschalenbildung) zeigt, daß auf der Kristalloberfläche vor dem Auftreten der Produktkristalle (Keimbildung oder Keimwachstum) eine dehydratierte Schicht gebildet wird. Die mikroskopischen Untersuchung zeigten auch, daß Reaktionen innerhalb des Kristalles ablaufen und daß die Produktbildung im gesamten Phasenvolumen erfolgt, gefolgt von einem Gitterzusammenbruch in Experimenten mit hohen Aufheizgeschwindigkeiten.

In Verbindung mit vorangehenden Ergebnissen erlauben uns diese neuen experimentellen Resultate die Formulierung eines Drei-Schritte-Mechanismus für die hier besprochene Umwandlung:
i) die Reaktion (Herauslösen von Wassermolekülen aus deren Gitterpunkten im Reaktanden);
ii) die Wanderung der durch die Reaktion freigesetzten Wassermoleküle durch die anfänglich gebildete, wasser-entquollene Schicht, die die Kristalle der Reaktanden umgibt;
iii) die Kristallisation einer solchen Schicht und Bildung des Produktes.