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Kinetics and Mechanism of the Dehydration of Crystal Hydrates

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The present review considers experimental data and the results of theoretical studies of the dehydration of crystal hydrates. The data have been systematised according to the stages of the reaction in the light of modern theories of the kinetics and mechanism of chemical reactions in solids. Attention has been drawn to a number of unsolved problems. It has been shown that the dehydration of crystal hydrates may prove a convenient model system in topochemistry for the solution of these problems. The bibliography contains 102 references.

CONTENTS

1. Introduction 919
2. Period preceding the formation of nuclei of the reaction product 919
3. Kinetics of the formation and growth of nuclei 920
4. Influence of various factors on the overall kinetics of dehydration 921
5. Theoretical description of the kinetics of dehydration 925
6. Mechanism of dehydration 926
7. Need for a study of the localisation of the dehydration of crystal hydrates 927

1. INTRODUCTION

Modern theories of the mechanism and kinetics of topochemical reactions are based to a large extent on experimental studies of the dehydration of crystal hydrates, since these processes provide a convenient model system which can be used to study the regular features of an important class of topochemical thermal decomposition reactions of the type:

$$A_{(solid)} \rightarrow B_{(solid)} + C_{(gas)}.$$

Moreover, the study of these processes is of independent interest, since many dehydration reactions (for example the dehydration of gypsum, alum, and metal sulphate penta- and heptahydrates) have important applications and are used in chemical technology, the technology of building materials, the metallurgical industry, etc.

Initially, the attention of many research workers was drawn to crystal hydrates by the apparent simplicity of their decomposition. As experimental data accumulated, however, it became clear that dehydration is in fact much more complex than previously supposed, and many facts relating to its mechanism have still not been explained. For example, it is not known why in many instances dehydration, having started at some point on the surface of a crystal, continues to develop at the same point (autocatalysis of the reaction); the factors responsible for the catalysis of dehydration by various additives, including the solid product, have not been determined; the relationship between the original structure and the structure of the product has been little studied, etc. Thus new studies of the mechanism and kinetics of the thermal decomposition of crystal hydrates are urgently required.

The aim of the present review is to systematise available data on the nature of dehydration and to draw attention to some problems which are not yet fully resolved.

Modern theories of the kinetics and mechanism of chemical reactions in the solid phase[1,2] show that the processes occurring in the dehydration of crystal hydrates can be divided into three groups: 1) the production of nuclei of the reaction product (prenucleation period); 2) the formation and growth of reactive nuclei; and 3) the overall kinetics of the process and the overall mechanism of the reaction.

It is obvious that this division is to some extent arbitrary, and that in real situations these three stages are mutually related. Nevertheless, we shall use it in the present review, chiefly for convenience in the presentation of the material.

2. PERIOD PRECEDING THE FORMATION OF NUCLEI OF THE REACTION PRODUCT

The study of the processes preceding the production of observable growing nuclei of the reaction product has been the subject of a comparatively small number of papers; this is due not to lack of interest in the study of this phenomenon, but to the complexity of the investigations. Most of the published papers, therefore, are concerned with the verification of theories regarding which imperfections in the crystal are responsible for the production of nuclei.

Existing theories of nucleation[3-5] relate chiefly to the thermodynamic conditions for their production and show little relation to the physicochemical features of the crystal. Almost no experimental studies of the factors responsible for the production of nuclei have been carried out, although they are of considerable interest.

In 1954, Garner and Jennings[6] suggested that as the water is removed, the defects formed on the surface of the crystal diffuse into its volume and accumulate at dislocations. In their opinion, the aggregates of defects formed in this way might act as centres for nucleus formation. The experimental test of this theory carried out by these authors using the dehydration of chrome alum showed, however, that the rate of diffusion of defects through the crystal is too low to have any significant influence on the rate of movement of the boundary between the starting material and its solid dehydration product.

Macdonald[7] pointed out that for reversible reactions, such as dehydration, it is difficult to imagine that the reaction can begin in the interior of a crystal. Even if such an act took place, the marked hindrance of diffusion at the point of development of the reaction would finally establish an equilibrium pressure, and the reaction would stop. Thus water molecules evaporating from the surface

at the points where they are least firmly bound to the crystal (point defects, impurities, dislocations, etc.) will form vacancies. The formation of nuclei in this instance will take place as a result of the migration of water molecules over the surface and their volatilisation at the points where vacancies were formed in the earlier stages.

The influence of dislocations on dehydration has been studied by many workers. As a result of such studies, Thomas and coworkers[8-10] concluded that if dislocations do have an influence on the dehydration of $NiSO_4.7H_2O$, they do so only in the earliest stages of the reaction. These early stages are naturally of particular interest in investigating the factors responsible for the production of nuclei, but it has not been possible to detect any significant correspondence between the points of emergence of the dislocations on the surface of a crystal and the points at which decomposition nuclei appear[8-11]. Moreover, it should also be noted that even if such a correlation were established, it would not provide an unambiguous answer to the question of whether the dislocations are themselves responsible for the production of nuclei, since dislocation pits in most instances consist of other point defects, impurity centres, etc.

Nevertheless, a relationship between the nuclei and the various imperfections in a crystal apparently does exist. This is indicated by experiments on the dehydration of $NiSO_4.7H_2O$,[12] in which a marked scatter was observed in the times at which the first nucleus appeared. Under the given conditions, in one of the experiments, the first nucleus (which usually appeared during the first hour) appeared only 495 min after the start of dehydration in a high vacuum. In another experiment, no nuclei appeared even 32 h after the start of the observations. On the other hand, if the surface of carefully prepared copper sulphate pentahydrate crystals is rubbed with a crystal of the monohydrate of the same salt, nuclei appear immediately in large quantities over the whole of the treated surface[13].

These few papers apparently contain all the available information which might provide an answer to the problem of the factors responsible for the production of nuclei. There is as yet insufficient experimental material to make it possible to relate the production of nuclei unambiguously to specific properties of a crystal and to predict the law governing the time dependence of the formation of nuclei.

3. KINETICS OF THE FORMATION AND GROWTH OF NUCLEI

The regular kinetic features of the appearance and growth of nuclei of the reaction product have been studied to a greater extent than the factors responsible for their formation. After the existence of nuclei had been clearly established, it was suggested that the induction period which is always observed in the dehydration of freshly prepared crystal hydrates is due chiefly to the anomalously slow rate of growth of the nuclei in the initial stages of the reactions[14,15].

To verify this theory, the rate of increase in the linear dimensions of the nuclei on $CuSO_4.5H_2O$ and $NiSO_4.7H_2O$ was measured[12,16]. It was found to be constant and approximately equal to the rate of propagation of the surface of separation, calculated from kinetic measurements of the loss in weight using the equations for a compressed parallelepiped (see below, section 5). The nuclei grew at a constant rate, however, only when the dimensions reached values of $(2-5) \times 10^{-3}$ cm. An analogous picture was observed in the study of chrome alum. In this instance, two kinds of nucleus were observed, each of which had its own constant rate of growth[17]. An induction period was also observed in this instance[18]. Table 1, taken from the paper of Cooper and Garner[17], gives data on the rates of growth of nuclei at different temperatures.

Table 1.

Temperature, °C	Rate of growth of nuclei $\times 10^6$, cm s^{-1}
35	8.64—8.89
30	6.04—5.85
25	4.03—3.84
20	2.22
15	1.20—1.11

It would be of interest to determine whether the nuclei grow into the interior of the crystal at the same rate or whether they have a planar shape and grow only over the surface of the crystal. From the kinetic viewpoint these two situations should differ fundamentally[2]. To resolve this problem for the dehydration of chrome alum, the extent of the development of nuclei was observed in a direction perpendicular to the surface, by cleaving the crystal and measuring directly the depth of penetration of the nuclei in partly dehydrated crystals. Two of these experiments on the dehydration of chrome alum at 30° gave rates equal to 7.8×10^{-6} cm s^{-1} and 5.9×10^{-6} cm s^{-1}, which agree with the values obtained by following their development over the surface (compare the data in Table 1). These results indicate that in some systems the rates of growth of the nuclei in directions normal to and parallel to the surface are equal.

In a study of the dehydration of potassium hydrogen oxalate hemihydrate, Hume and Colvin[19] observed the interesting phenomenon of an arrest in the movement of the surface of separation; this could not be explained at the time. In their experiments, the nuclei of the product grew at a constant rate until they reached a certain size, after which growth stopped. After 5–10 min, growth of the nuclei began again, and the rate of growth was equal to that before the arrest.

A constant rate of growth of the nuclei has been observed in almost all studies of the decomposition of crystals. The kinetics of the growth of nuclei is thus described by a linear function of time, beginning from dimensions of $\sim 10^{-3}$ cm.

It was noted above[12] that a marked scatter is observed in the times at which the first nucleus appears on different single crystals of the same substance. Despite this feature, however, the curves obtained by plotting the number of nuclei against time are smooth (Fig. 1). These curves are described to a high degree of accuracy by the equation

$$\lg N = k \lg (t - t_i),$$

where t_i is the time at which the first nucleus appears. The existence of this relationship suggests that although the appearance of the first nucleus is apparently a random process, depending on a large number of factors, the crystal apparently subsequently undergoes irreversible changes which predetermine the times at which the second, third, etc. nuclei appear. In other words, the

time at which the $(n + 1)$th nucleus appears is determined unambiguously by the presence of the n nuclei previously formed on the surface of the crystal.

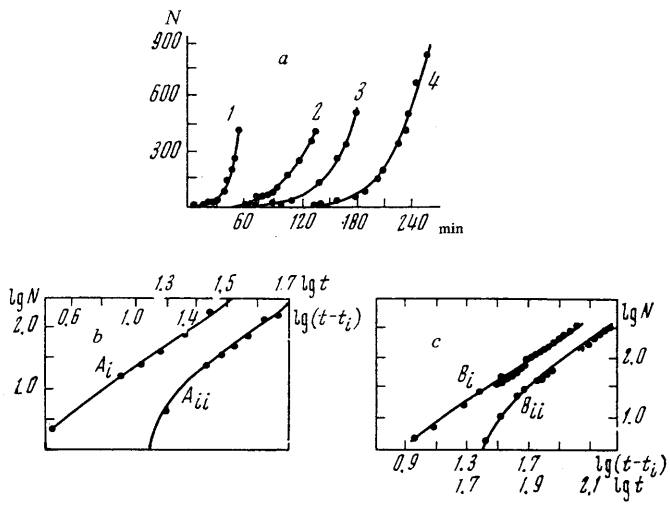


Figure 1. Time dependence of the number of nuclei at different temperatures: 1) 22°; 2) 15°; 3) 8°; 4) 1° (a), and the same curves on logarithmic coordinates: A_i, B_i—plots of $\lg N$ against $\lg(t - t_i)$ (b); A_{ii}, B_{ii}—plots of $\lg N$ against $\lg t$ (c).

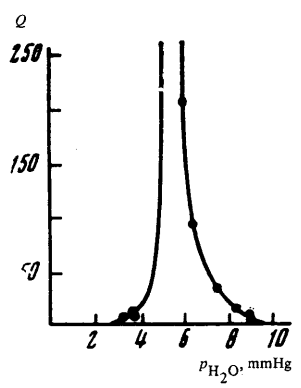


Figure 2. Dependence of the ratio of the maximal rate of formation of nuclei at a given water vapour pressure to the rate of nucleus formation in a vacuum (Q) on the water vapour pressure.

The presence of water vapour alters the rate of formation of nuclei on different crystal hydrates in different ways. If a crystal is treated with water vapour after it has been kept for some time in a vacuum, the rate of nucleus formation at first increases, and then decreases, passing through a maximum. This has been observed for $KCr(SO_4)_2.24H_2O$, $NH_4Cr(SO_4)_2.24H_2O$, and $CuSO_4.5H_2O$.[6] All these hydrates showed a sharp increase in the number of nuclei when the vessel was evacuated again. This effect has not been explained, although it is of undoubted interest. It is difficult to relate it to the blocking action of water vapour on the crystal surface, if we consider the nature of the relationship between the water vapour pressure and the ratio of the maximal rate at a given water vapour pressure to the rate of nucleus formation in a vacuum, given in Fig. 2 for the example of chrome alum. In contrast to the situation for chrome alum, the rate of nucleus formation in the dehydration of, for example, potassium aluminium alum is almost independent of the water vapour pressure in the space surrounding the crystal.

The influence of water vapour on the rate of movement of the surface of separation or, which is the same thing, on the rate of increase in the linear dimensions of the nuclei will be discussed below.

4. INFLUENCE OF VARIOUS FACTORS ON THE OVERALL KINETICS OF DEHYDRATION

In the kinetic approach to the study of solid-phase reactions, the degree of transformation of the substance (from the loss in weight or liberation of gas) during decomposition is usually measured. The curves obtained in this way are integral with respect to all parameters except time. More complete studies of reactions of this type have shown that the rate of dehydration depends markedly on a large number of factors. Some of these factors are structural (the dependence of the rate on the crystal habit, the degree of dispersion, the defect character of the lattice, etc.), and their influence on the decomposition has been described[20,21]. Another group of factors which must be taken into account in the study of the kinetics of the decomposition of solids is directly related to the general regular features of solid-phase reactions. In the present section, we shall examine these features as they apply to the dehydration of crystal hydrates.

Self-cooling. All crystal hydrates which have been studied lose water in a markedly endothermic process. As a consequence, on dehydration in a vacuum, when heat exchange between the specimen and the thermostat takes place chiefly by radiation, the temperature at which the removal of water takes place may generally speaking not be equal to the temperature of the thermostat. This feature has been pointed out by many workers. The effect has been described as self-cooling, and calculations based on the theory of black-body radiation have been proposed to take account of it. For example, in the dehydration of $CuSO_4.5H_2O$, Smith and Topley[22] suggested that the temperature of the crystal be calculated by means of the expression:

$$\lambda\left(-\frac{dm}{dt}\right) = S \cdot 1.38 \cdot 10^{-12}[T^4 - T'^4]$$

which allows for the physical characteristics of the crystals. Here λ is the heat of the reaction, $(-dm/dt)$ the mass rate of the reaction, S the external surface area of the specimen, and T and T' the temperatures of the thermostat and the specimen respectively.

An analogous equation was used by Cooper and Garner[17] in a study of the dehydration of alum:

$$\lambda\delta\Delta = k\Delta_0[T^4 - T'^4]$$

where k is Planck's constant, Δ_0 the initial surface area from which radiation takes place, Δ the surface of separation at a given moment of time, and δ the reaction rate

in g $cm^{-2}s^{-1}$. The self-cooling effect is not small enough to be neglected without distorting the true decomposition picture. The magnitude of this effect, calculated from the equation for chrome alum[17], is given in Table 2.

Table 2.

Cooling Δt, deg	Temperature of thermostat, °C
11.8	35
8.8	30
6.2	25
4.1	20
2.3	15

The results show that even at 15°, the extent of the self-cooling is much greater than the generally accepted limits of temperature stability in an isothermal process. Neglect of this effect may lead to significant errors in the determination of the kinetic parameters of a reaction.

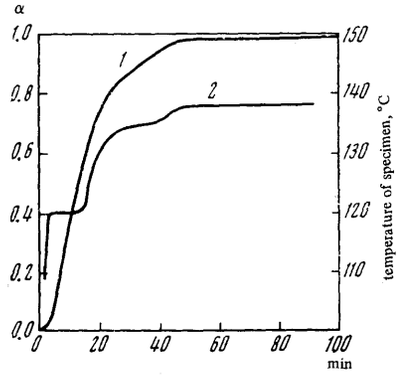


Figure 3. Simultaneous change in the loss in weight (1) and temperature (2) on the dehydration of $CaSO_4.2H_2O$ (temperature of thermostat 138°).

The question of the true conditions under which a reaction takes place naturally requires the most thorough analysis. For this purpose, experiments have been carried out in which the temperature of a specimen and its degree of transformation were recorded simultaneously[23,24]. An example of the results is given in Fig. 3. The simultaneous recording of the temperature and the degree of decomposition was carried out for the dehydration of $CaSO_4.2H_2O$. A noteworthy feature is that the temperature of the thermostat (138°) was not attained even as $\alpha \to 1$. Most of the specimen (see Figure) decomposed at an almost constant rate at ~ 120°. In this instance, equalisation of the thermal fluxes—the rate of supply of heat from outside and the rate of absorption of heat in the reaction—apparently took place. This conclusion appears the more correct since the reaction takes place at the surface of separation between the original hydrate and its decomposition product, so that heat exchange takes place through a surface which is also the reaction zone.

In this example, the dehydration of gypsum was carried out at a water vapour pressure equal to 200 mmHg. Despite the presence of a gaseous atmosphere facilitating heat exchange between the specimen and the thermostat, however, the effects of self-cooling were significant in this instance also. There thus appears to be little justification for the assertion[22] that in a gaseous environment the effect of self-cooling can be neglected.

In most instances, the curves for the topochemical decomposition of solids are S-shaped[1]. The latest studies[25,26] apparently prove that for reactions with marked endothermicity, such as the dehydration of crystal hydrates, the magnitude of the induction period on the $\alpha(t)$ curves depends to a large extent on the conditions of heating of the crystals.

Special mention must be made of the determination of the rate of dehydration from the rate of movement of the boundary of separation between the phases. In most instances this has been determined from some kinetic equation for a fixed value of α and has been related to a temperature calculated for the given value of α with allowance for the effect of self-cooling. This determination is correct, however, only if quasi-steady-state conditions obtain for the process. In other words, the change ΔT in the temperature of the specimen within a certain small time interval should be sufficiently small compared with the corresponding change $\Delta\alpha$ in the degree of transformation of the specimen during the same time interval:

$$\frac{\Delta T}{T} \ll \frac{\Delta\alpha}{\alpha}$$

where T and α relate to the middle of the time interval. If this condition is not observed, thermographic conditions will be established, so that the values of the kinetic parameters will differ from those obtained under isothermal conditions[26,27].

Influence of the gaseous atmosphere. The gaseous atmosphere in which the dehydration of crystals takes place may be inert or contain water vapour. Direct experiments have established that an inert atmosphere, up to pressures of 3–4 mmHg, has no significant influence on the rate of dehydration[28]. Above this pressure, diffusion control begins to have an effect, and perturbations associated with the presence of the inert atmosphere in the system become significant. It is very difficult to establish the nature of this influence, since it is superimposed on other effects and cannot be isolated in pure form.

Under dynamic conditions, the extent of the influence of an inert atmosphere depends on the rate of gas flow in the reaction zone. This problem has not been studied systematically, although there are indications that the rate of dehydration increases with increase in the rate of gas flow[29-31].

The presence of water vapour in the reaction zone influences the observed rate of dehydration. This is observed first because the rate of dehydration represents the difference between the actual rates of the forward dissociation and back reactions, and secondly because these opposed rates are themselves functions of the concentration of molecules in the reaction zone. They are determined by adsorption equilibrium. The relationship between the reaction rate constant (or constants) and the partial pressure of water vapour may therefore be very complicated, and it is complicated even further by the fact that water vapour may have a direct catalytic effect on the dehydration and also on the subsequent crystallisation of the product.

Topley and Smith[32], and Volmer and Seydel[33], in studies of the dehydration kinetics of manganese oxalate dihydrate, observed a complex relationship between the rate constant and the partial pressure of water in the reaction system, characterised by the presence of a maximum and a minimum on the plot of rate against H_2O pressure. Other crystal hydrates usually showed only a smooth decrease in rate with increase in pressure[34].

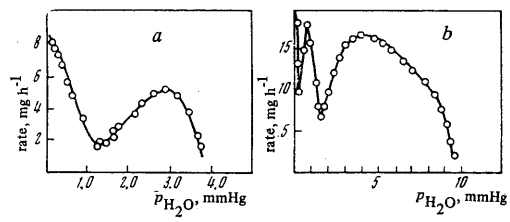


Figure 4. Dependence of the rate of dehydration on the water vapour pressure for $MnSO_4.4H_2O$ (a) and $ZnSO_4.7H_2O$ (b).

For a long time, manganese oxalate was regarded as unique in this respect. A systematic study of the phenomenon showed, however, that with increase in the water vapour pressure, most crystal hydrates behave in approximately the same way as manganese oxalate, and in some instances in even more complex fashion[35-37]. The relationships for the crystal hydrates $MgSO_4.4H_2O$ and $ZnSO_4.7H_2O$ are given in Fig. 4. For zinc sulphate, the rate of dehydration passes through two minima and two maxima with increase in the water vapour pressure, whereas magnesium sulphate tetrahydrate shows approximately the same behaviour as manganese oxalate.

A study[37] of the dehydration of various crystal hydrates at a fixed water vapour pressure in the surrounding atmosphere showed that at a certain pressure after the initial act of nucleus formation the reaction stopped completely (Fig. 5).

It is difficult to find an unambiguous interpretation of this complex behaviour of crystal hydrates on dehydration in the presence of water vapour. The shape of the curves obtained by plotting rate against pressure is usually attributed to competition between the accelerating action of water on the crystallisation of the product and the retarding action on the movement of water through the layer of product into the surrounding space[34,35]. In some instances the phenomena associated with the presence of water in the reaction zone are attributed to the formation of porous structures in the decomposition zone[38]. The difficulty of finding an explanation is due chiefly to the lack of experimental data on the adsorption equilibrium of water during the decomposition.

The existence of gaseous catalysis has been verified experimentally[39] for $CuSO_4.5H_2O$. Study of the dehydration in a stream of hydrogen in the presence of small quantities of water and HCl showed that the reaction rate is increased considerably (by a factor of 5–7). Analysis of the partly decomposed crystals showed that HCl is adsorbed by the surface of the crystals. These experiments demonstrate again the need for a study of the phenomena of adsorption and desorption of water by the surface of crystal hydrates during their decomposition.

The "impedance" of the layer of product. As the reaction develops into the interior of a crystal, the layer of product may finally become so thick that diffusion controls the removal of water molecules into the surrounding space from the surface of separation of the phases, which is also the place where the reaction is proceeding. This effect has been detected by many authors[22,28,39,40] in the study of dehydration, and has been called "impedance".

The magnitude of the impedance effect is measured as the difference between the observed rate of movement of the surface of separation into the interior of the crystal for a given layer thickness and the corresponding rate for zero thickness. Since the rate of movement of the surface of separation at zero layer thickness cannot be measured directly, it is found by extrapolation to zero layer thickness[41]. Strictly speaking, this extrapolation should be not to zero thickness but to the thickness corresponding to the maximal rate of movement of the surface of separation, since in the initial period after their production, the nuclei grow at an anomalously slow rate. This applies equally to the development of the reaction zone into the interior of the crystal in the initial stages of the reaction.

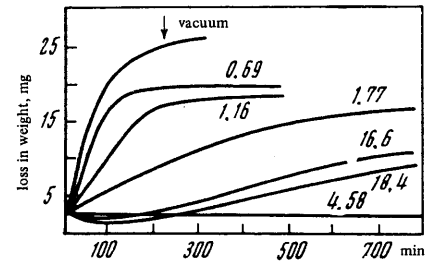


Figure 5. Dehydration curves for $MgSO_4.7H_2O$ at various water vapour pressures (given by the figures next to the curves). Decomposition does not take place at p_{H_2O} = 4.58 mmHg.

Despite the importance of an understanding of the phenomenon of impedance in the study of the kinetics and mechanism of dehydration, there is still lack of agreement on this subject. Taylor and Taylor[42] found that the product obtained in a comparatively thin layer has a high porosity, so that it could hardly have had a significant influence on the reaction rate. Nevertheless, they do not reject the possibility that water molecules adsorbed on the surface of the product may hinder considerably the removal of water from the reaction zone into the free volume. This may in turn be responsible for an increase in the water vapour pressure in the reaction zone and hence a decrease in the reaction rate.

Generally speaking, all explanations put forward for the origin of the impedance reduce in one way or another to a displacement of the equilibrium at the surface of separation between the starting material and the product. From the kinetic viewpoint, this question is probably closely related to the range—kinetic or diffusion—in which the reaction takes place.

We noted above that theories of the competition between the catalytic action of water on the crystallisation of the product and the retarding influence (as a consequence of diffusion) of the layer of product have been used to explain the "strange" dependence of the rate of dehydration on the water vapour pressure. From this it may be concluded that the diffusion and adsorption properties of the product cannot be neglected, but the extent to which they are significant is not yet known.

The phenomenon of impedance has also been used many times to explain the familiar so-called autocatalytic course of the curves for solid-phase decomposition (see Vorontsov's review[43]). The impedance effect possibly does not always apply, as far as can be judged from experiments on the measurement of the rate of growth of nuclei into the interior of a crystal[18]. Finally, it should be noted that for strongly endothermic dehydration, a decrease in the rate of propagation may also be due to a change (decrease) in the flow of heat supplied to the reaction zone as a consequence of differences in the thermal conductivity of the starting material and the product. An amorphous product in this instance may even act as a heat insulator.

The above examination shows that impedance is a complex phenomenon. Despite its small magnitude, neglect of the effect in the study of the dehydration of crystal hydrates may lead to significant errors in kinetic determination and to incorrect interpretation of reaction mechanisms.

Formation of Labile Phases and Intermediate Liquid Hydrates

Partington in 1911 suggested[44], and a large number of subsequent studies subsequently proved[33,39,45,46], that the dehydration of crystal hydrates, particularly at low partial water vapour pressures, gives an intermediate product amorphous towards X-rays. The absence of lines on the X-ray diffraction patterns for specimens dehydrated in a vacuum can be due entirely to the true amorphous character of this product. On the other hand, as pointed out by Roginskii[47], the product formed on dehydration in a vacuum may consist of a disordered assembly of very fine crystals (up to 10^{-7} cm in cross-section), and this would also lead to the absence of lines on the X-ray diffraction patterns, because of the insufficient sensitivity of the apparatus. Subsequent electron-microscope studies by Roginskii and coworkers[48] showed, however, that despite marked dehydration of $Na_2SO_4.10H_2O$ and $MgSO_4.7H_2O$ crystals at a pressure of 10^{-4} mmHg, the external form of the crystal and its ultramicroscopic structure initially remain unchanged.

It was only on prolonged irradiation that cavities were produced on the surface and a tendency for new cavities to be produced close to those previously formed (localisation) was observed. Some time after the start of the appearance of the cavities, the crystal consisted of a fine network of solid material surrounding the cavities produced, that is a skeletal structure appeared, indicating an amorphous intermediate product, rather than a submicrocrystalline product.

The problem of the formation of intermediate unstable phases has been most fully studied by Khomyakov[49] and Frost and coworkers[50]. Thus Khomyakov observed that partly dehydrated crystals of $CuSO_4.5H_2O$, immediately after the experiment was stopped, liberated a quantity of heat (4824 cal $mole^{-1}$) approximately equal to the difference between the heats of the dehydration of the freshly prepared and partly decomposed $CuSO_4.5H_2O$ crystals. According to Thomsen[51], these heats are −17334 cal $mole^{-1}$ and −12519 cal $mole^{-1}$ respectively, and their difference does indeed differ little from the heat determined by Khomyakov. This effect was not observed on repeated dehydration.

Frost carried out analogous experiments and followed the quantitative change in the amorphous product during the reaction at different water vapour pressures. He found that after the removal of water, the product remaining liberated heat for a definite time interval. This thermal effect was attributed to rearrangement of the structure from an amorphous state to a crystalline state corresponding to the structure of the product. Thus it was found that the intermediate amorphous products are rich in energy, and are metastable phases. The values of the heats of the transformation from the intermediate state to the final state, taken from a paper by Frost and coworkers[38], are given below:

$ZnSO_4.H_2O$(amorphous) → $ZnSO_4.H_2O$(crystalline); ΔH = −7600 cal $mole^{-1}$
$CuSO_4.H_2O$(amorphous) → $CuSO_4.H_2O$(crystalline); ΔH = −7170 cal $mole^{-1}$
$MgSO_4.H_2O$(amorphous) → $MgSO_4.H_2O$(crystalline); ΔH = −6550 cal $mole^{-1}$
$NiSO_4.H_2O$(amorphous) → $NiSO_4.H_2O$(crystalline); ΔH = −4720 cal $mole^{-1}$
$CoCl_2.H_2O$(amorphous) → $CoCl_2.H_2O$(crystalline); ΔH = −1390 cal $mole^{-1}$

(it is indicated in parentheses whether the compound is in the amorphous or crystalline state).

It was found that from a certain pressure, almost no amorphous product is produced on dehydration in water vapour. The values of these critical pressures are very close to those corresponding to the minimal rate on the plots of the rate of dehydration against H_2O pressure. Not all of the crystal hydrates form an amorphous intermediate product even on dehydration in a vacuum. For example, salts such as $NiNO_3.6H_2O$, $Mg(NO_3)_2.6H_2O$, and chrome alum, on dehydration in a vacuum, form a crystalline lower hydrate with an extensive internal surface due to formation of capillaries, whereas dehydration in the presence of water vapour at ordinary pressures, as with the other crystal hydrates, gives normal crystalline aggregates. An attempt to classify hydrates according to this characteristic was made in a review by Dell and Wheeler[52].

All the phenomena described above can be explained as follows: within a certain temperature range, the lattice framework is preserved even after the crystal (for example $CuSO_4.5H_2O$) has lost four water molecules. This also favours the flow of the water diffusing through the layer of product. The lattice framework is preserved until nuclei of the new stable phase appear. The production of these nuclei depends on the decrease in the flow of water through the layer of monohydrate and also on the temperature and surrounding pressure of water vapour.

Studies of the nature of the amorphous product and its role in the decomposition of crystal hydrates are of particular interest in relation to theories of the localisation of the reaction in a narrow zone at the surface of separation between the starting material and the product. Since the specific volumes of the original hydrate and final product are not always the same, the layer of amorphous product then will always compensate the structural stresses and ensure the structural change from the starting material to the reaction product.

The existence of intermediate lower hydrates has been established from vapour pressure isotherms[53,54], and their formation on thermal dehydration has been detected

in a large number of thermographic [55,56] and X-ray diffraction [57-70] studies.

The importance of thermographic investigations in the study of the kinetics of dehydration should not be overemphasised. Reisman and Karlak [58] showed that small changes in the conditions under which thermographic experiments are carried out produce a marked scatter in the experimental results obtained. This is in fact the reason for the frequently encountered lack of agreement in the thermographic results obtained by different authors. Thermographic studies are of greatest value in the discussion of the mechanisms of the dehydration of crystal hydrates, when, as we shall subsequently see, it is absolutely essential to allow for the formation of intermediate lower hydrates during the decomposition.

The intermediate hydrates are extremely unstable, and this explains the almost complete lack of information on the kinetics of their dehydration in pure form. Nevertheless, Cooper and coworkers [71] were able to study the kinetics of the dehydration of copper sulphate trihydrate. The kinetic curve which they obtained differs little from the usual curve for solid-phase decomposition.

Influence of the addition of the solid product. Since dehydration takes place at the surface of separation between the original hydrate and its product (usually a lower hydrate), the possibility of direct contact between the starting material and the amorphous or crystalline lower hydrate cannot be excluded. In this connection, the possible catalysis of the dehydration by solid decomposition products is of undoubted interest. Studies of this kind have been made by Rae [14], Skramovsky [55,72], and Vallet [30], and later by Sakovich [73] in an examination of the decomposition of hydrated salts of copper, cobalt, and magnesium.

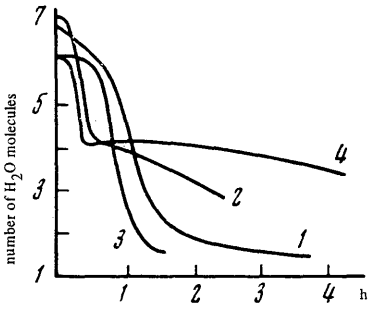


Figure 6. Dehydration curves for $CoSO_4.7H_2O$ and $CoSO_4.6H_2O$ in the pure state and with the addition of anhydrous salt: 1) $CoSO_4.7H_2O$; 2) $CoSO_4.7H_2O$ + 5% $CoSO_4$; 3) $CoSO_4.6H_2O$; 4) $CoSO_4.6H_2O$ + 5% $CoSO_4$.

These studies showed that the addition of a lower hydrate increases the stability of that intermediate hydrate and at the same time increases the rate of the stage leading to the formation of the salt added. This is illustrated by the curves, taken from Feitknecht's paper [69], for the dehydration of cobalt sulphate hexa- and heptahydrates containing 5% of the anhydrous salt (Fig. 6). According to Sakovich [73], the observed accelerating action of the added product on the dehydration of crystal hydrates is due to their interaction at the points of contact with the surface layer of the starting material. This interaction is due to the affinity of the reaction product for water vapour, the pressure of which is always greater above the original hydrates than above their dehydration products. Introduction of the additive produces regions of the reaction zone are produced even at room temperature, and this apparently leads to an increase in the rate of the process. This explanation is supported by a comparison of these experiments with Garner's observations of the formation of nuclei on the surface of copper sulphate pentahydrate treated with the monohydrate of the same salt, when nuclei appeared almost instantaneously.

The partial stabilisation of the intermediate hydrates added to the starting material, observed by Vallet [30], can be attributed rather to a simple increase in the quantity of intermediate phase.

The problem of the mechanism of the accelerating action of the added product is closely related to a more general problem in the chemistry of solids—the mechanism of the influence of various heterogeneous additives on solid-phase reactions. This problem is at present far from being solved, despite its obvious importance for topochemistry.

5. THEORETICAL DESCRIPTION OF THE KINETICS OF DEHYDRATION

The problem of the satisfactory description of the kinetics of dehydration has faced research workers since the earliest studies of these processes, and cannot be regarded as fully resolved. The first attempts to provide a quantitative description of dehydration were based, strangely enough, on the idea of autocatalysis [74,75]—an idea which has in fact been revived recently [76]. Historically, however, the development of modern topokinetics originated in the successful application of Langmuir's idea [77] that the surface of separation between the phases is the point at which reaction takes place to the description of the kinetics of decomposition of various hydrates [41].

In fact, the possibility of describing the kinetics on the basis of simple geometric representations of the form of nuclei and their number appeared very attractive. This simplicity proved to be deceptive, however. Hume and coworkers [78] examined three examples of topochemistry, differing radically in their mode of description. In the first, nuclei are formed immediately and cover the surface of the particle almost completely. The process is then described by the equation of a "contracting" sphere, parallelepiped, etc., depending on the shape of the crystal. In the other extreme case, when the frequency of formation of the nuclei is low compared with the rate of movement of the surface between the phases, the reaction obeys a unimolecular law, as for example in the conversion of monoclinic into orthorhombic sulphur. The example of greatest interest for topochemistry is the intermediate situation, where the ratio of the rate of production of nuclei to the rate of movement of the surface between the phases is such that at sufficiently small degrees of conversion, each particle will contain at least one nucleus. In this instance the reaction rate will pass through a maximum and an S-shaped curve will result. It is this third possibility which is usually realised in the decomposition of crystal hydrates.

One of the first equations used for the description of the kinetics of dehydration was an equation in which the

mass rate, divided by the original surface area of the crystal[22], was taken as the rate constant. Subsequently transformed into the equation of a compressed parallelepiped, it was used successfully by Hume and Colvin[28] to describe the kinetics of the dehydration of copper sulphate pentahydrate. A number of other equations[29,40,78], some simpler, some more complex, including the Polanyi–Wigner equation, have been applied to various reactions, with varying success.

With the development of the formal kinetics of reactions in the solid phase, more complex equations based on various physical models of the reactions have appeared. Thus a more important problem, in our view, is the applicability of the kinetic method of analysis to the determination of the mechanism of a reaction, or in other words the problem of the correspondence between the model used in the derivation of the kinetic equation and the real physical picture of the decomposition. Molony and Ridge[80], in a study of the kinetics of the dehydration of calcium sulphate dihydrate, found that the experimental results are described equally effectively by the equations

$$A - B(1-\alpha)^{1/3} = kt$$

and

$$A - B(1-\alpha)^{1/2} = kt$$

(naturally, with different constants). The correlation coefficients calculated for the two equations were −0.969 and −0.983 respectively, that is they almost coincided. In the opinion of these authors[80], this result provides an example of a situation in which applying the equations of formal topokinetics in itself cannot provide as a criterion for the unambiguous selection of one of two or more proposed reaction mechanisms. This conclusion applies not only to dehydration, but to topochemical reactions in general, and forms the basis of a contradiction between a real process and the method used to describe it. The efforts of many research workers have been directed towards the elimination of this contradiction. Some have adopted the approach of increasing the accuracy of familiar equations by including the distribution of particle sizes[81,82], by making allowance for mass and heat transfer in the crystal[83], by using the activated-complex theory[84], etc. Others consider that there is no point in trying to describe the entire decomposition curve by means of a single equation, since different stages of the process correspond to different mechanisms[85]. Despite all efforts in the field of the kinetics of dehydration, however, two of the anomalies noted by Garner[86] as early as 1938 have not yet been explained satisfactorily.

a. The reaction rate in a large number of examples of the decomposition of solids, including the decomposition of crystal hydrates, increases as a very high power of time. The exponent is much greater than might have been expected from simple theoretical considerations based on the theories of the boundary of separation.

b. The reaction rate in the initial stage is proportional to the mass of sample decomposed, and not its area.

It may therefore be definitely stated that the problem of an adequate description of dehydration is generally speaking a part of topokinetics, which is at present largely unsolved.

6. MECHANISM OF DEHYDRATION

We noted above that the dehydration of crystal hydrates involves the formation of intermediate amorphous or crystalline lower hydrates. This feature determines the possible decomposition schemes.

The transitions between the different stages of the reaction have been studied most fully for $CuSO_4.5H_2O$ and $CaSO_4.2H_2O$. When the reaction takes place in a single stage, for example from copper sulphate pentahydrate to the monohydrate, the reaction scheme can be represented in the form shown in Fig. 7.[17,40,87]

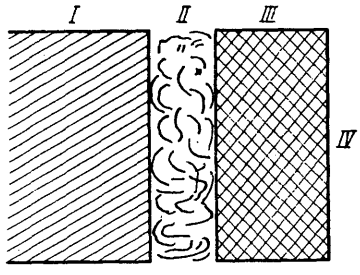


Figure 7. Dehydration of crystal hydrates: I) reagent; II) intermediate layer; III) product, undergoing slight recrystallisation; IV) open space (vacuum or water vapour).

Garner and Pike[88], referring to data on the structure of $CuSO_4.5H_2O$,[89] point out that dehydration in a vacuum, which always gives the monohydrate, corresponds to the loss of four water molecules coordinated to the copper atom. The fifth water molecule is not coordinated, and the strength of its bonding is apparently different. Their non-equivalence in the $CuSO_4.5H_2O$ lattice is also indicated by experiments on isotopic exchange[90].

In the presence of water vapour, the decomposition is complicated considerably, chiefly because of the production of the trihydrate as an intermediate compound. According to Colvin and Hume[34], the overall scheme for the dehydration of copper sulphate pentahydrate can be represented in the form:

$$CuSO_4 \cdot 5H_2O \rightarrow \underset{\text{amorphous}}{CuSO_4 \cdot 3H_2O} \begin{cases} \xrightarrow{I} CuSO_4 \cdot H_2O + 2H_2O \\ \xrightarrow{II} \underset{\text{crystalline}}{CuSO_4 \cdot 3H_2O} \xrightarrow{III} CuSO_4 \cdot H_2O + 2H_2O \end{cases}$$

The amorphous trihydrate formed in the decomposition, when treated in a vacuum, immediately loses two more water molecules (route I) and is converted into the monohydrate. The presence of water vapour may direct the reaction along route II → III, since water facilitates the crystallisation of the amorphous trihydrate.

The activation energy for the dehydration of $CuSO_4.5H_2O$ and $CuSO_4.3H_2O$ has the values E_1 = 16–18 kcal mole^{-1} [17] and E_2 = 15.6 kcal mole^{-1} [71] respectively, that is the difference is not large.

The various stages in the dehydration of $CaSO_4.2H_2O$ are given in the following scheme[91]:

$CaSO_4 \cdot 2H_2O$ (monoclinic)

Dehydration, possibly including topotaxy ↓ ↑ Recrystallisation without topotaxy

$CaSO_4 \cdot \frac{1}{2}H_2O$ + water (rhombohedral)

Quasi-zeolite dehydration of the lattice without recrystallisation ↓ ↑ Adsorption of water from vapour, quasi-zeolite reaction

$CaSO_4$ Soluble anhydrite.

↓

$CaSO_4$ Orthorhombic anhydrite

This compound is also of interest since the mechanism of its complete dehydration is complicated by an additional transformation between the two crystalline forms of the anhydrous salt[92].

It is impossible to give here all the crystal hydrate decomposition schemes which have been proposed: the number is greater than the number of hydrates. The examples given show sufficiently clearly the importance of making allowance for the stepwise character of the overall process and the formation of various intermediate compounds in the description of dehydration.

7. NEED FOR A STUDY OF THE LOCALISATION OF THE DEHYDRATION OF CRYSTAL HYDRATES

We have already mentioned various unsolved problems in the chemistry of crystal hydrates. In the present section we would like to consider particularly the problem of the localisation and auto-localisation of the process. As already mentioned in the introduction, we are referring to the interesting property of crystal hydrates and other topochemical systems of decomposition with the formation and growth of nuclei. It is extremely important to answer the question of why this takes place and to find methods of controlling this process. The importance stems primarily from the large number of practical applications of crystal hydrates on the one hand, and also from the considerable theoretical importance of the problems of localisation in topochemistry on the other hand, since the concept of nuclei forms the chief distinguishing feature of topochemical reactions.

An example of the practical utilisation of the results of these studies is provided by the production of catalysts by the dehydration of crystal hydrates. Partly dehydrated crystal hydrates are at present used as catalysts for a large number of industrial reactions[93,94]. In this connection, the control of the formation and growth of nuclei would open up the possibility of controlling the properties of the catalysts obtained, through the directed production of the catalytically active materials. This of course is not the only field in which it is important to find ways of controlling localised processes. They are equally important in photography, metallurgy, etc.

The problem of localisation naturally is not specific for dehydration alone. It can be applied equally successfully to any solid-phase reactions involving the formation and growth of nuclei of the product. It is convenient, however, to distinguish crystal hydrates from most other similar systems since it is at present difficult to find a class of substances which have been studied in such detail. In addition to a very large number of studies of the kinetics and mechanism of the dehydration of crystal hydrates, detailed structural studies have been made[70], the infrared spectra have been studied[95,96], dehydration has been studied by NMR[97] and dielectric spectroscopy[98], and data have been obtained by isotopic substitution[99] and from proton conductivity in crystal hydrates[100] and from the influence of ultrasonic radiation on the dehydration[101]; the absolute velocities of water molecules leaving a crystal surface on dehydration have also been measured[102]. These studies have been so extensive and varied because crystal hydrates provide one of the best model systems in topochemistry, by means of which it may be possible to come close to a solution of the problem of localisation; the importance of this problem in theory and practice has already been emphasised.

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