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State of Water in Inorganic Crystal Hydrates and the Characteristic Features of Their Dehydration

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The state of water in inorganic crystal hydrates has been discussed, and the various distortions of the water molecule, as far as its dissociation, under the influence of the environment have been analysed. The reactions involved in the extensive dehydration of crystal hydrates have been examined from the viewpoint of the relationship between the state of water in the hydrate and the characteristic features of the dehydration processes leading to irreversible changes in the substance undergoing dehydration and to the decomposition of a complex oxo-anion. The bibliography contains 221 references.

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I. INTRODUCTION

The nature and state of water in hydrated compounds has recently been attracting increasing attention from research workers. This is due to the part played by hydrates in the solution of general problems of solid structure and also to the considerable practical importance of these compounds, since many substances can be obtained most readily and in purest form as the crystal hydrates. In technology and preparative chemistry, in addition to the original hydrates, extensive use is also made of their dehydration products. For example, one possibility being discussed is the provision of water for cosmonauts by the dehydration of water-containing non-terrestrial minerals.

The variety of substances capable of combining with and firmly retaining water to some extent predetermines the variety of ways in which water can be bound. Moreover, the way in which the experimental results from the study of hydrates are presented often depends on the methods used and the aims of the work. This has apparently been responsible for the extreme variety of terms characterising the nature and the state of water in inorganic hydrates, which has led almost to a state of crisis in the present nomenclature for the types of water in hydrates. The chief among these are: 1) sorbed or hygroscopic (adsorption and capillary) water [1-3]; 2) water of crystallisation [1,4,5]; 3) water of constitution [1,6-8]; 4) structural water [9-11]; 5) hydrolysis water [12]; 6) lattice and non-lattice [13]; 7) layer and inter-layer [14]; 8) combined [15] and chemically combined [16]; 9) constructional [17]; 10) zeolite [18]; 11) peripheral [19]; 12) high-temperature [20]; 13) hydrate [21]; 14) oxonium [22-24]; 15) intercrystal-polyamorphionic [12]; 16) coordination [25]; 17) clathrate hydrate water [26], etc. To these should apparently be added the various forms of "anomalous water" [27-29], which are apparently stable only in the layer next to the wall in

capillaries, so that they can also be regarded as a special type of combined water [30]. If allowance is made for the fact that the varied forms of water in hydrates differ significantly from one another only in the limit, the indefinite nature of each of the above terms becomes clear. This indefinite character leads to the temptation to create "one's own" new terms, characterising "most fully" the state of water in specific materials.

As far as dehydration reactions are concerned, a considerable amount of work, particularly early work, has been carried out without an analysis of the real state of water in the substance, and the "anomalies" frequently observed in experiments, for example the removal of fractional quantities of water, have been regarded as "contrary to common sense" and have therefore been ignored [31]. The discussion of the kinetics and thermodynamics of dehydration processes often does not make allowance for the structural and even chemical changes in the solid phase on dehydration. If however these changes are too obvious, attempts are made to create attractive thermodynamic models without allowance for the actual processes taking place in the solid substances on heating. At the same time, a fairly large amount of experimental material has now accumulated, showing that the water molecule is not always present in a hydrate as an individual structural unit, that dehydration is often accompanied by the partial or even complete decomposition of the salt, and that in many instances this process is the primary process and not, for example, the hydrolysis of the salt by water vapour. This leads to the conclusion that the water in a solid substance has a unique reactivity, and the behaviour of water in the dehydration of a hydrate is evidently determined to a considerable extent by its spatial and energetic structure in the original hydrate. Information of this type has become available chiefly in the last ten years, as a consequence of the fruitful application of modern physical methods of study to the examination of hydrates.

The present review attempts to summarise the available data and to establish the relationship between the state of water in an inorganic hydrate and the characteristic features of its dehydration. Recognising that it is not appropriate to include in the present review a large number of sharply differing classes of water-containing substance, we shall restrict ourselves to an examination of so called crystal hydrates, that is phases with definite compositions, exhibiting physical and chemical individuality, with molecular compositions usually represented in the form $X.H_2O$. Particular attention will be paid to hydrates containing an oxo-anion, to an analysis of the various distortions of water in a hydrate lattice under the influence of the crystal field and intermolecular interactions, as far as its dissociation, and also to the decomposition of the complex oxo-anion of a salt on the dehydration of its hydrate.

2. METHODS OF STUDYING THE STATE OF WATER IN CRYSTAL HYDRATES

The most important methods for studying the structure of crystal hydrates are X-ray diffraction and neutron diffraction, for which the achievements in the determination of the symmetry and molecular parameters of compounds are familiar. With reference to the problems being discussed, it may be noted that despite the fact that the position of the hydrogen atom in a hydrate is determined from X-ray diffraction data with a low accuracy or is derived from general geometric considerations, the results obtained in this way by careful work in most instances show good agreement with the results obtained by neutron diffraction. When comparing the numerical data obtained by these methods, however, it must be borne in mind that O–H distances determined by X-ray diffraction are always shorter than those determined by neutron diffraction [32]; this is due not to the error in the measurements but to the difference in the nature of the quantities measured. Moreover, the shortened O...O distance found by X-ray diffraction in water-containing substances (less than the sum of the van der Waals' radii) does not always provide a sufficient criterion for concluding that there is hydrogen bonding in the substance [33,34].

The state of water in a crystal becomes more definite when the results of a structural analysis are compared with the results obtained by measuring quantities directly related to the strength characteristics of the chemical bond; in this field, a leading position is rightly occupied by the vibrational-rotational spectra of molecules—the infrared absorption and reflectance spectra and the Raman spectra (RS)—since these reveal the characteristic frequencies of the molecular vibrations, which depend in definite fashion on the geometry of the molecules and the strength characteristics of the chemical bond. When the molecule is perturbed by some external influence, the force constants of the chemical bond are altered, and this brings about a regular displacement of the bands in the vibrational spectra. These methods have been found to be particularly useful in the study of water-containing compounds, because of the comparative ease of isotopic replacement of hydrogen and the large (~1.4) coefficient of isotopic displacement of the frequencies of the vibrations of the groups of atoms containing hydrogen.

The vibrational spectra of water in various states have been the subject of a fairly large number of reviews and monographs on the infrared spectra of water in inorganic substances in adsorbed, zeolite, crystallisation, constitutional, and free forms [35,36], the librational vibrations of water in solid hydrated compounds [37], the spectroscopy of hydrogen bonds involving water [38–42], and the spectroscopic manifestation of coordinated water [36,43–45]. For the purposes of further discussion, we shall deal briefly with the most characteristic manifestations of water in vibrational spectra in relation to its state.

The stretching vibrations of the O–H groups in the monomeric gaseous water molecule have frequencies of 3650 cm^{-1} (ν_1) and 3750 cm^{-1} (ν_3). Polymerisation by H-bonds in the gaseous phase or conversion into the condensed state leads to a displacement of the absorption bands towards longer wavelengths, accompanied by broadening of the bands until they merge. There are a large number of empirical and semi-empirical correlations between the values of the νOH frequency and the length of the H-bond, [38,46–49] between the length of the H-bond, the potential curves, and the hydroxyl frequencies [50]; between the magnitude of the displacement $\Delta\nu$OH and the energy of the H-bond; [39,51–53] and between the frequency νOH and the electronegativity of the hydrate-forming element [54]. In the calculation of the displacement of the bands, the origin is usually taken as the ν_3 frequency of the non-perturbed water molecule or the averaged value 3700 cm^{-1}, since even when there are two bands in the νOH region, a reliable assignment to ν_1 or ν_3 is difficult. Calculations by means of empirical equations relating the length and energy of the H-bond to the displacement $\Delta\nu$OH often give satisfactory results even in the study of substances of different types, differing in chemical character

and crystal structure, as a consequence of the marked sensitivity of νOH to the configuration of the H-bond. These relationships are usually linear, if the length of the H-bond lies in the range 2.5–2.8 Å. There is as yet no sufficiently convincing criterion for selecting the limiting O...O distance in a H-bridge, at which interaction of the H-bond type can be neglected, since $\Delta\nu_{OH}$ approaches zero asymptotically in the range 2.9–3.4 Å. The value 2.84 Å in the frequently used expression:

$$\Delta\nu_{OH} = 4.43 \cdot 10^3 \cdot (2.84 - R) \quad (1)$$

where R is the O...O distance, in our opinion, is too low, since a distinct displacement of the absorption bands is observed even for much larger distances. Bellamy[48] proposed the more appropriate value 3.35 Å, beyond which, according to various theoretical considerations, the energy of the interaction should not exceed 0.2–0.3 kcal mole^{-1}. This quantity appears in the semi-empirical expression

$$\Delta\nu(\text{cm}^{-1}) = 50\left[\left(\frac{d}{R}\right)^{12} - \left(\frac{d}{R}\right)^{6}\right] \quad (2)$$

used in calculations covering a wide range of H-bond lengths. The energy of the H-bond can be estimated with sufficient accuracy by means of a relationship established from a large number of results, according to which one unit of energy in kcal mole^{-1} is equivalent to a change in frequency of 50 cm^{-1}. More accurate values can be obtained only for groups of substances of the same type, and always require verification by some independent method.

In view of the highly characteristic nature of the stretching vibrations of the OH groups, this range of the spectrum does not make it possible to obtain unambiguous information on the nature of the oxygen–hydrogen group in a solid substance, since the ranges corresponding to the νOH bands of hydroxide ions OH^-, molecular water H_2O, and the hydrated proton $H_{n+2}O_m^+$ overlap. This problem can be resolved by analysing the bending vibrations of the hydrates, for which the frequencies lie below 1500 cm^{-1} for OH^-, in the range 1590–1680 cm^{-1} for H_2O, and in the range 1680–1800 cm^{-1} for the hydroxonium ion H_3O^+.[55,56] The frequency of the bending vibration of an isolated water molecule is 1595 cm^{-1}. On association, including that due to H-bonding, the absorption band corresponding to this vibration is displaced towards higher frequencies[57], but the displacement is much smaller than that for the stretching vibrations, and for the same perturbation amounts to 10–50 cm^{-1}. The number of components of the bending band coincides with the number of forms of water molecule in the original hydrate, but unfortunately this criterion can be used only when the degrees of binding of the molecules differ considerably, since in most instances, because of the small displacement of δ_{H_2O}, the bands due to different kinds of water are not resolved.

The above regular features apply qualitatively for all substances, irrespective of their nature and state of aggregation. In the analysis of the bonding of water in inorganic hydrates from their infrared spectra, however, it is necessary to make allowance for the fact that coordination of the water molecules to a metal ion influences the vibrations of the molecules in the same way as H-bonding. The displacement of the bands due to the stretching vibrations of water towards longer wavelengths for strong electrostatic complexes as a consequence of the coordination of water to a metal, according to calculations, may reach 600 cm^{-1}, and is determined by the polarising and electron-accepting properties of the cations[58]. A rigorous separation of the perturbing influence of each of these two factors on the vibrations of water molecules is hardly possible, since on the one hand, hydrates in which the existence of H-bonding might be excluded are as yet unknown, and on the other hand, the effects of coordination and H-bonding are closely related, since the polarisation of the O–H bond in the field of the cation, by increasing the proton-donating properties of water, leads to a decrease in the force constant of the bond, and this is equivalent to an increase in the strength of the H-bond and a correspondingly greater displacement of ν_{OH}. Definite progress in this direction has been made in a study of the infrared spectra of series of isomorphous perchlorates[59–61], since the perchlorate ion is one of the weakest proton acceptors. These results show that in this class of compound, the value of $\Delta\nu$OH resulting from the coordination of water, even for *d* elements, is not more than 150 cm^{-1}.

The introduction of water into the first coordination sphere of a metal leads to the production, in the vibrational spectra of the hydrates, of bands characterising the vibrations of $M(H_2O)_n$ complexes, at comparatively high frequencies. The M–O stretching vibrations in these groups are observed in the range 300–500 cm^{-1} for a number of aquo-complexes[62], and at higher frequencies for small ions with high charges; for example, the bands for $[Be(OH_2)_4]^{2+}$ and $[Al(OH_2)_6]^{3+}$ lie at 860 cm^{-1} and 600 cm^{-1} respectively[63,64].

Promising possibilities for the theory of the energy of H-bonding are provided by the analysis of the vibrational spectra of the H-bond itself; these spectra are produced as a result of the loss of rotational or translational degrees of freedom by the molecules of groups of atoms on formation of the H-bond. The vibrations of the hydrogen bond are observed in the frequency ranges 100–200 cm^{-1} for the stretching vibrations, and 50–80 cm^{-1} for the bending vibrations. Unfortunately, since the use of long-wave infrared spectrometers is not yet widespread, work in this field has been carried out chiefly by Raman spectroscopy, and this has restricted the range of substances studied to solutions and single crystals. Attempts have been made[65–71] to compare the frequencies with the lengths of H-bonds, but the state of water of crystallisation in this range of the spectrum has as yet been insufficiently studied, and no definite generalisations can be reached.

Difficulties in the Interpretation of the Infrared Spectra of Water in Crystal Hydrates

A clear distribution of the vibrations of water in different states in different regions of the spectrum is characteristic only of limiting ideal situations. As already noted, the nature of the spectrum in the range of the stretching vibrations of the OH groups does not make it possible to determine the nature of the oxygen–hydrogen group in the substance. The production of several bands in this frequency range can be related not only to the existence of several kinds and states of water but also to the formation of H-bonds with different energies by the same molecule, and also to the production of overtone, combination, and resonance frequencies. In this instance, partial deuteration of the substance, which makes it possible to determine the nature of the splitting of the OH bands, is extremely useful. At the same time, the absence of appreciable structure in a band does not indicate uniformity of the binding of water in a substance, since the vibrations of groups of different character may not be resolved, as a

consequence of the large width of the band due to a hydroxyl group forming an H-bond. Moreover, it must be borne in mind that the band frequently observed at 3450 cm^{-1} may be due not to the substance being studied but to the absorption of water adsorbed by the substance, particularly for substances with a highly developed surface. Fortunately, the low sensitivity of the position of this band to the nature of the sorbing substance facilitates its assignment [72].

In our opinion, considerable care must be exercised in the use of the repeatedly recommended method for the quantitative determination of different types of water in a substance by partial dehydration until a particular component of the spectrum disappears [55,73]. This method can be adopted without significant reservations only for substances of the zeolite type, since, as will be shown below, the state of water changes during the dehydration of a salt. This is particularly true of aquo-complexes.

The bending vibrations of water in a number of hydrates may be observed at frequencies of ~1670 cm^{-1}, and their assignment to molecular water or the hydroxonium ion becomes difficult. In this instance an unambiguous interpretation can also be carried out by studying partly deuterated materials. Allowance must be made, however, for the fact that in a number of substances the degree of hydration of the proton may be greater than unity, and this is also reflected specifically in the nature of the spectrum and must be taken into account in its interpretation [74]. Situations more difficult to explain are those in which the frequency of the bending vibration of water in a hydrate is displaced towards longer wavelengths relative to its position for monomeric water, and the structural data exclude the possibility of formation of hydroxo-compounds [75-78]. This may be due to a significant change in the angular characteristics of the water molecules. Thus in magnesium sulphate monohydrate the distance between the protons is 1.65 Å compared with the usually observed 1.50–1.58 Å, [76,79] and for $CuCl_2.2H_2O$ the HOH angle increases to 111.36°. [80]†

Although the analysis of the spectra in the stretching and bending ranges has shown that the water molecule retains its vibrational individuality, this does not exclude the possibility that bending vibrations of M–OH groups are produced when water is present in the first coordination sphere of an electron-accepting metal and its position is determined by the nature of the complex-forming metal.

The interpretation of the characteristic vibrations of an aquo-complex is most complicated, since this range corresponds to the stretching and bending vibrations of a large number of oxo-anions, and more particularly since deuteration has little influence on the positions of the bands of an aquo-polyhedron.

NMR and other methods. Considerable progress in the study of the state of water in hydrates has been made in recent years by proton magnetic resonance (PMR) and ^{17}O nuclear magnetic resonance (NMR) spectroscopy [42,44,81-83].

† It may be that the vibrational spectrum of water in aquo-complexes with H-bonding does not correspond to the triatomic model usually employed, and that the production of several bands in the range 1400–1600 cm^{-1} is due to the production of additional degrees of freedom in the vibration of, for example, a penta-atomic fragment of the type $M-O\begin{matrix}H\ldots O^- \\ H\end{matrix}$.

The PMR method has given important information on the lifetime of the H-bond and, most important, it has confirmed directly that in systems with H-bonding there is proton exchange in the O–H...O group, with a comparatively low activation energy (2–7 kcal $mole^{-1}$) [84,85] and has shown that reorientation and rotation of a molecule of water of crystallisation as a whole are possible [86-89]. An important feature for the understanding of the mechanism of the dehydration of a number of compounds is that the mobility and free path of a delocalised proton along the chain of H-bonds in ice have been found to be much greater than those in liquid water [90]. These quantities are even greater in clathrate hydrates [91], that is the stabilisation of the bonds by the lattice facilitates proton transfer.

Since the PMR method gives information primarily on protons, its use for the study of the state of water as a whole is somewhat limited. In the determination of the coordination of water to a metal ion it is preferable to study ^{17}O NMR, and this method has been used, in particular, to study the hydrate numbers of a number of metal ions. Unfortunately, this information has been obtained chiefly for the liquid state. For solid hydrates, for which low-resolution resonance is chiefly employed, its achievements have been much more modest. For a restricted range of substances, various empirical correlations have been found between the inter-proton distance and the length of the H-bond [83], but these relationships require verification for a wider range of substances and by other independent methods (vibrational spectra, structural analysis, etc.).

Other methods for studying the state of water in a solid, for example measurement of the dielectric properties, spectroscopy in the visible and ultra-violet ranges, magnetochemical methods, and EPR spectroscopy, are much less specific, and their application to the problem being considered is limited to several individual instances. If water is coordinated to a cation, however, these methods may give extremely useful additional information, particularly for the hydrates of salts of the transition metals.

3. STRUCTURE OF CRYSTAL HYDRATES

The mechanical, physical, and chemical properties of crystal hydrates are determined to a considerable extent by the position and state of the water molecules in their structure. At this stage, therefore, a general classification of hydrates, taking account of all the properties of the water-containing substance, is hardly possible. Any attempt to generalise the properties of large groups of hydrates must be based primarily on the final aims of the generalisation. From this viewpoint, for a description of the geometric arrangement of the water molecules relative to the other components of the crystal, it is quite satisfactory to use the classification adopted in crystal chemistry [92], based chiefly on Bernal's theories [93]; in this classification, all hydrates are divided into the following groups: a) hydrates in which the water molecules are isolated from one another; b) hydrates with isolated unit structures, in which water forms independent groups; c) chain hydrates; d) layer hydrates; e) hydrates with three-dimensional frameworks formed by water molecules. In the examination of dehydration reactions, however, this classification can be taken only as a first approximation, since it does not reflect the variety of forms of water and the influence which this has on the chemical properties of a

real hydrate, in which the water molecules interact strongly with the cation and anion of the salt and with one another, undergoing much greater distortion not only relative to their configuration in the gaseous phase, but also relative to water in the solid and liquid states; for example, in aquo-complexes the M–OH_2 distance is extremely close to or equal to the M–O distance in the corresponding oxide [94].

Since in most instances the analytical data do not give information on the forms in which water is present in a substance, it is necessary first of all to have criteria for distinguishing water of crystallisation from water of constitution, that is water present in ionised form, for example as hydroxide or hydroxonium ions. Since neutron diffraction techniques are not widely available, and X-ray diffraction does not give unambiguous results when applied to water, a suitable criterion for an extremely wide range of substances is provided by the presence of the band due to the bending vibration of molecular water in the vibrational spectrum of a hydrate, since the position of this band is highly sensitive to the conversion of water into the ionised state. Thus crystal hydrates can be regarded as substances in which the water molecule retains its vibrational individuality.

For the discussion of the state of water in crystal hydrates in relation to their dehydration, it is convenient to divide them into the following groups: 1) substances for which the hydrate number (n) is greater than the coordination number (CN) of the metal in the given compound; 2) hydrates with n equal to the coordination number; 3) hydrates with n less than the coordination number. As proposed by Shishkin [95], hydrates with variable composition, of the zeolite type, form an independent group of hydrates containing molecular water.

Many hydrates with a large quantity of water of crystallisation can be represented as solid solutions of water and the corresponding anhydrous salt, since their structure, with some assumptions, can be interpreted as corresponding to the structure of ice in which the positions of some of the water molecules and the cavities are occupied by ions of the salt. The nature and position of the bands in the infrared spectra of these hydrates in the range of the water vibrations are close to those in the spectrum of ice, and their heats of dehydration are also close to the heat of sublimation of ice.

When n is greater than the coordination number by one or two units, two structurally non-equivalent types of water can be clearly distinguished: part of the water, in quantities corresponding to the coordination number of the metal, is present in its first coordination sphere, and the rest of the water is present at a considerable distance from the cation (~4 Å). This situation is observed in many metal heptahydrates and in copper salt pentahydrates, and has been confirmed by direct structure determinations, from the bands due to water in the infrared spectra, and by NMR. [96–100] The water not combined with the metal forms H-bonds with a coordinated water molecule, or, if the steric conditions are favourable, with the anion; the energy (~4.5 kcal $mole^{-1}$) and length of these bonds are often independent of the nature of the anion, as shown by the presence, in the infrared spectra of these hydrates, of a band at ~3400 cm^{-1}, close to ν_{OH} for molecules bound by H-bonds in liquid water. This molecule has a much greater mobility than coordinated water [101].

The properties of water from the immediate environment of a metal are determined chiefly by its interaction with the cation and anion, and to a smaller extent by the interaction with water outside the coordination sphere, so that they are of the same type as those of hydrates of the second group. Hydrates in which the hydrates numbers are equal to the coordination number and in which all the water is in the inner coordination sphere of the metal (aquo-complexes) make up a large group among known inorganic crystal hydrates. The energy of the H-bond formed by coordinated water can vary over a fairly wide range (the value of $\Delta\nu_{OH}$ sometimes reaches 1000 cm^{-1} [102,103]), depending on the nature of the cation and anion. Ionic aquo-complexes in a solid substance undergo various distortions under the influence of the crystal field and the H-bonds, so that the water molecules among themselves and the OH groups of an individual molecule can become non-equivalent; this is often accompanied by the production of different M–OH distances, the difference amounting to 0.02–0.2 Å for neighbouring water molecules [94,104]. If the symmetry of the crystal is sufficiently high or a large number of states of water molecules with similar energies are produced, this non-equivalence may not lead to splitting of the bands in the infrared spectra, and more or less broadened single bands are observed in the range of absorption of water. With marked distortion of the coordination polyhedron, however, for example as a consequence of the Jahn–Teller effect or on formation of H-bonds of different energies by the same water molecule, the bands due to the stretching and sometimes also the bending vibrations of water may be split, and the water becomes spectroscopically non-uniform.

The most complicated sets of possible energy states of water molecules and positions in the structure are shown by the hydrates of the third group, containing a small quantity of water of crystallisation. At the same time, this class of hydrate is of greatest interest for the solution of the problems of preparing anhydrous substances, since as a consequence of the stepwise nature of the reactions, the dehydration of higher hydrates in the final stages gives products with small and sometimes fractional hydrate numbers.

If the water in these hydrates is present in the first coordination sphere of the metal, the coordination polyhedron also contains some oxygen atoms of the anion, so that in addition to the M–OH interaction there may also be interactions of the H-bond type between water and the anion of another polyhedron, leading to marked distortion of the water molecule itself and of its environment. Thus for nickel nitrate tetrahydrate [105], eight different O–H...O distances have been found, and each of these bonds produces its own absorption band in the infrared spectra in the range 3525–3130 cm^{-1}, the dependence on RO...O being given by the empirical function (1). For a definite mutual spatial orientation of the water molecule and the anion, both hydrogen atoms of water may be joined to the same oxygen atom of an anion, and this leads to a decrease, relative to liquid water and ice, in the inter-proton distance and hence in the HOH angle [97,106,107]. On the other hand, one of the hydrogen atoms may remain almost free, whereas the other takes part in the formation of a strong H-bond [108]. The angular characteristics of the water then undergo distortions which are the opposite of those in the first example, and the vibrations of the two OH groups can be regarded as almost independent. Thus the above correlation between the length of the H-bond and the inter-proton distance may have only a limited application for systems of this kind.

Lower hydrates sometimes show anomalous values for the frequencies of the water vibrations [109], unusual coordination [110,111], and fractional hydrate numbers. All these facts indicate that many lower hydrates, particularly

those obtained by the dehydration of higher hydrates, are in a stressed state; this may be attributed to some lack of correspondence between the small size of the cation and its extensive coordination possibilities and the large radii of the complex oxo-anions. This lack of correspondence is removed to a considerable extent for aquo-complexes, as a consequence of the increase in the effective radius of the complex aquo-cation. On this basis it should be expected that the decrease in the hydrate number as far as the formation of the anhydrous salt should be accompanied not only by the distortions of the water molecule noted above but also by an increase in the extent of the perturbing influence of the lattice on the anion.

The distortion of the symmetry of an anion can be followed by direct structure determinations, and also from the splitting of degenerate absorption bands and the appearance of forbidden bands in the vibrational spectra. For example, on going from copper sulphate pentahydrate to the monohydrate, the symmetry of the anion decreases [112] from T_d to C_{3v}, or to C_{2v} in the dehydration of the double sulphates of various transition metals [113] and even to C_s for the selenate anion, with the same symmetry, on going from the hexahydrate to the dihydrate in double copper selenates [114]. This situation is typical, and has also been noted for rare earth metal bromates [115], phosphates [116], and many other salts. An increase in the complexity of the spectra in the range of the vibrations of the anion may naturally be due not only to a decrease in the symmetry of the anion but also to a decrease in the site symmetry of the crystal, but in a number of instances these effects can be distinguished fairly simply [117]. Moreover, for systems in which the influence of the symmetry of the lattice can in practice be excluded, for example for ion exchange films, decrease in the degree of hydration is accompanied by a sharp increase in the magnitude of the splitting of the bands due to the degenerate vibrations of sulphate and selenite anions [118]. A number of authors have not noted any significant differences in the infrared spectra of higher and lower hydrates [119] or have observed a decrease in the complexity of the spectrum in the range of the vibrations of the anion on going from hydrates to the anhydrous salts [120,121], and this has led to the suggestion that H-bonds have a decisive influence on the decrease in the symmetry of the anion. Calculation of the stability of solid systems with H-bonds [122] has shown, however, that the rupture of the O–H...O bond is energetically more favourable than distortion of the valency angles of the anion, despite the fact that the linear H-bond is the most stable [123]. In the limit, this leads to a situation in which some hydrogen atoms in crystals may not take part in the formation of a H-bond. It appears that H-bonding in a hydrate under favourable conditions intensifies the decrease in the symmetry of the anion brought about by more powerful interactions. This is confirmed by the fact that when an anion is coordinated to a metal ion, the splitting of the bands due to the degenerate vibrations is accompanied by their displacement towards longer wavelengths [113,124,125]. Thus those instances where the symmetry of an anion increases with decrease in the hydrate number are to be regarded as exceptions, particularly since the decrease in the complexity of the spectrum is often only apparent, as a consequence of the conversion of the substance to the amorphous state on dehydration.

On the basis of the nature of the interaction of water with a metal ion, it should be expected that the strength of the $M-OH_2$ bond should be determined primarily by the polarising and electron-accepting properties of the cation, that is by its size, charge, and outer electronic structure. In a series of elements of the same type, ν_{OH} for water decreases regularly with decrease in the radius of the ion or with increase in its charge [126,127]. When several factors change simultaneously, however, it becomes difficult to predict the relative strength of the interaction of water with the cation. Thus $\Delta\nu_{OH}$ is much greater for hydrated salts of aluminium and beryllium than for zirconium and hafnium compounds. For transition metals, the degree of binding of water is greater than might have been expected for a purely electrostatic interaction. Within the first transition series, $\Delta\nu_{OH}$ and hence the degree of perturbation of the water molecules in the salts of the doubly-charged ions decrease in the order: $Mn < Co < Ni < Cu > Zn$, which corresponds closely to the familiar Irving–Williams series for the stability of complex compounds. The magnitude of the splitting of the degenerate vibration of the anion changes in the same order, indicating that the mechanisms of the interaction of the cation with water and the oxo-anion are similar.

The extent of the distortion of water under the influence of the anion is characterised by the proton-acceptor properties of the latter. Study of the hydration of anions introduced into an ion-exchange film based on polystyrene (R) has shown that these properties change in the opposite order to the abilities of the corresponding acids to undergo protolytic dissociation [128], increasing in the order RSO_3^-, $RSeO_3^-$, RPO_3^{2-}, $RSeO_2^-$, RPO_2H^-. In accordance with this, ν_{OH} in the spectrum of their hydrates decreases from 3465 cm^{-1} to 3335 cm^{-1}, indicating that the strength of the H-bond increases in the same order. Unfortunately, an unambiguous interpretation of the influence of various cations and anions on the state of water is possible only for strictly isomorphous series, which is not always possible, or in the study of ion-exchange films, although in the last instance it is not always possible to achieve reliable control of the degree of hydration. Despite this, the order of change in the energy of the H-bond with change in the nature of the anion, observed by Karyakin and Muradova [103] for substances of different types, where the energy increases from 1.7 kcal $mole^{-1}$ to 8.5 kcal $mole^{-1}$ in the series ClO_4^-, NO_3^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}, shows satisfactory qualitative agreement with the above order for the polystyrene acids.

Thus if we take as a measure of the influence of the cation the change in ν_{OH} relative to ν_{OH} for a similar hydrate of an alkali metal salt, and as a measure of the influence of the anion the magnitude of $\Delta\nu_{OH}$ relative to the perchlorate of the same element (assuming that the effects of the two factors on water are additive), we find that for a series of hydrates the frequency of the stretching vibrations of water should be displaced to 3000 cm^{-1}, which corresponds to a H-bond energy of about 15 kcal $mole^{-1}$, that is a value close to the energy of a chemical bond. The state and reactivity of water combined in this way must naturally differ significantly from those for the free state.

This should lead primarily to a marked increase in the degree of protolytic dissociation of water. Hydrated metal ions in solution exhibit acidic properties to a greater or lesser extent, as a result of dissociation to form hydrogen ions and a complex hydroxoaquo-ion. According to Schwarzenbach [129], water in the inner coordination sphere of metal complexonates can be titrated with alkali. Water of crystallisation can react with metals with which liquid water does not react [130]; a remarkable feature is that compounds with small hydrate numbers are much more active than the higher hydrates.

Modern theories of the energetics of H-bonding and the structure of substances containing hydrogen bonds make it

possible in many instances to explain the state of water in a hydrate and to predict its possible chemical properties. For substances with strong intermolecular interactions we can expect in the limit the production of a symmetrical O...H...O band, so that the proton belongs with equal probability to the water molecule and the anion, and this formation should acquire the properties of an acid salt. From the general course of the relationship between O–H and O...O distances, it follows that this situation should arise for an H-bond length of about 2.3 Å. This value is assumed in the discussion of various models of "anomalous" water or poly-water [131,132] and appears to have been confirmed experimentally [133]. In a number of solid substances a symmetrical hydrogen bond has been assumed at much larger distances [134–137] (of the order of 2.4–2.5 Å). In systems with longer H-bonds there is also a definite probability of transfer of a proton from water to the anion, since the potential curve for an unsymmetrical bond has two minima for which the height of the potential barrier may be reached on thermal excitation, and the efficiency of this process can be increased by an appreciable factor by tunnelling of the proton along the H-bond. According to calculations [138], this process is probable for a distance between the minima reaching 0.8 Å.

If a system of H-bonds is formed by several water molecules, the energy barriers to the removal of a proton may be decreased by the positive heat of formation of oxonium ions. In accordance with this, the state of water in iron phosphate and arsenate dihydrates is more accurately represented by the formula $MXO_4.(OH)^-H_3O^+$ than by the classical formula with isolated water molecules [139,140]. Oxonium ions have been found in the solid state in a number of hydrates of inorganic acids and salts [103,141–145]. According to Zundel and Metzger [146], a proton is completely removed from polystyrene sulphonic acid at a degree of hydration equal to two, that is when the ion $H_5O_2^+$ is formed. This ion has also been detected in hydrogen chloroaurate tetrahydrate [147], where the distance between the potential wells is 0.62 Å, and in perchloric acid dihydrate [148], where it is assumed that there is only one minimum on the potential curve. It is suggested [149] that the oxonium ion is most stable in the form of the trisolvate and that its hydrate should have the structure $H_9O_4^+$. According to Lundgren and Olovsson [150], this ion is present in hydrobromic acid tetrahydrate. Hydrated hydroxonium ions with the composition $H_3O^+.(H_2O)_n$, where n reaches 10, have been detected by mass spectrometry in the gaseous phase. Despite the fact that the $H_9O_4^+$ ion has been assigned [154] the planar symmetrical structure $H_3O^+.3H_2O$ (H-bond energy 46.3 kcal mole^{-1}), the heats of hydration of the hydroxonium ion found from the mass-spectrometric data do not show an inflection at n = 3, but show a smooth change, and at n = 7 they approach the heat of evaporation of water from a flat surface [155]. The structure $H^+(H_2O)_n$ is therefore to be preferred. A remarkable feature is that the geometric structure and energetics of the hydrated proton and hydroxide ion almost coincide for equal degrees of hydration [156].

In these complex formations, despite the fact that molecules of water of crystallisation often retain their individuality as vibrational units, the proton is completely delocalised over the entire ion. In the limit, as shown by Shakhparonov [157,158], many properties of aqueous systems can be described by assuming that a conductivity zone exists for protons. Although the concepts of a proton gas have been applied chiefly to liquid systems [159], it will be shown below that they have proved useful for the explanation of various characteristic features of the dehydration of solid inorganic hydrates.

Finally, for the salts of multiply-charged readily hydrolysed metals, the water may be completely dissociated, and these compounds should be regarded as complex acids, and not crystal hydrates. Nevertheless, many substances of this type are still classified as crystal hydrates, apparently because of the difficulty of determining the true state of water in the materials. A number of properties of solid hydrates of various zirconium and hafnium salts, however, make it impossible to regard these compounds as crystal hydrates or as the corresponding acids, which exist in solution. For zirconyl chloride hydrates, structures with oxo-bridges or hydroxo-bridges, or structures with complex polynuclear ions of the type $[Zr_4(OH)_8.(H_2O)_{16}]^{8+}$, [160,161] have been proposed. A tendency for hydrated compounds of this type to form bridging groups and to acquire more strongly acidic properties is shown by tin phosphates [162], aquopolytungstates [163], metal borates, etc. In these limiting situations, the water is present as water of constitution, and the suggested criterion for estimating the state of water does not apply.

In most hydrates, however, the state of water is characterised by a greater or lesser displacement of hydrogen ions towards the anion, and the magnitude of this displacement is determined by the properties of the cation and anion, and also by steric factors. In this connection, the corrections to the formulae of hydrates proposed by a number of authors on the basis of the vibrational spectra [for example for magnesium carbonate trihydrate [164,165] $Mg(OH)^+(HCO_3)^-.2H_2O$] must evidently be understood not as corresponding to complete dissociation of the water molecule but as an illustration of the fact that the water molecule reacts so strongly with the anion that a change in its vibrational characteristics becomes possible. To the same extent this is also true of Lendormy's conclusions [166] that many transition metal sulphate monohydrates should be regarded as acid salts of the type MH_2SO_5.

The tendencies, noted above, for the state of water in crystal hydrates to change with change in the hydration numbers and the nature of the environment relate primarily to systems in which all or part of the water is in the coordination polyhedron of the metal. There are therefore some exceptions, where the water in lower hydrates is less firmly bound than that in higher hydrates. This situation is observed in calcium sulphate hemihydrate [167], in which the water must be regarded as zeolite water, since the structure remains unchanged on dehydration. The interpretation of the spectra of hydrates of this kind in the far infrared range has been based on a crystal structure model [168] in which water forms a molecular lattice which is quasi-independent of the ionic lattice of the salt.

4. DEHYDRATION OF CRYSTAL HYDRATES

The extensive range of dehydration reactions has produced a large number of papers on the study of these reactions, but up to the present there has been no sufficiently well-founded approach to the interpretation of many experimentally established features of these reactions in relation to their kinetics or to the problems of the thermal stability of the intermediate hydrate forms produced in the decomposition of the original hydrate. To some extent this can be attributed to the variety of forms in which water is combined in solid inorganic hydrates, and also to the specific nature of the problems studied and hence of the conditions under which the experiments have been

carried out, and this has made it difficult to compare the results of different studies, even of the same substance.

In their monographs, Young [169] and Garner [170] have discussed a large number of studies of the kinetic features of dehydration. In many of these, sufficient attention has not been paid to the possible influence of the formation of various intermediate hydrates on the kinetic characteristics. On the other hand, the operations involved in the isolation of individual hydrated phases and the determination of their thermodynamic functions make it necessary to take account of kinetic factors, because of the ease with which false equilibria are established in hydrates. Only in a few papers have the macro-kinetic characteristics of a reaction been related to the energetic and geometric structure of water in the hydrate lattice.

In most instances, dehydration takes place in stages, and the number of intermediate phases may be extremely large. Thus in the dehydration of magnesium sulphate heptahydrate, seven intermediate hydrates are formed [171,172]. It is only in a few instances, chiefly when water is not combined with the metal, that it can be removed from water-rich hydrates in a single stage. Most of the intermediate forms are generally produced in the final stages of the process, often with the formation of compounds with fractional hydrate numbers which sometimes are not submultiples of the original number. Fractional hydrate numbers are sometimes also encountered in hydrates precipitated from solution under normal conditions [173], for example $CdSO_4.\frac{8}{3}H_2O$, so that there are insufficient grounds for assuming that these compounds should be regarded as solid solutions of the anhydrous salt and the corresponding hydrate. The number and composition of the intermediate hydrates depends to a marked extent on the nature of the substance and the conditions under which the reaction is carried out. They may be different even for isomorphous substances, for example aluminium sulphates [174] and selenates [175], or rubidium and caesium tellurites [176]. Measurement of the vapour pressure over hydrated strontium oxalate showed that in the range of hydrate numbers from 2.5 to 2 there exists a series of non-stoichiometric hydrates, for which the heat of dehydration [177] increases from 12.7 kcal mole^{-1} for $n = 2.5$ to 17.7 kcal mole^{-1} for $n = 2$. An increase in the heat of dehydration with decrease in the hydrate number is a common feature of most hydrates. The effective activation energy of the reaction changes in the same order, and in many instances it is close to the heat of the reaction. The differences sometimes observed in these quantities, or their anomalously high values (particularly for ΔH calculated from the vapour pressure) are often related to the possibility of formation of unstable intermediate compounds or to the increased energy of the final dehydration product. The values of these quantities also depend to a marked extent on the particle size of the original crystals. Thus the dehydration of goethite [178] is endothermic for the coarsely-crystalline material, athermic when the particle size is about 100 Å, and exothermic for specimens with a smaller particle size. Engberg [179] has shown that if the activation energy and heat of dehydration are determined for monodisperse particles with the same dimensions, the values are almost equal.

The conditions of the process, particularly the pressure and composition of the gaseous phase, have a marked influence on the chemistry of dehydration. For example, with change in the external water vapour pressure from 10 mmHg to 80 mmHg, the number of stages and the composition of the intermediate phases in the dehydration of strontium oxalate changes three times [177]. Examples are known where processes become more complicated [174] or simpler [180,181] (with reference to the number of stages) in a vacuum and at atmospheric pressure. The temperature dependence of the equilibrium vapour pressure above all possible intermediate hydrates in a given system does not always make it possible to predict the sequence of stages for given specific conditions, since the influence of kinetic factors may lead to the production of thermodynamically unstable compounds as the chief product.

To some extent, the state of the dehydrated product also depends on the external pressure. It has been shown by a complex thermal and X-ray diffraction study [182] that in the dissociation of copper sulphate pentahydrate at pressures above 15 mmHg the loss of water is synchronous with the change in crystal structure; with decrease in pressure, the rate of crystallisation differs to an increasing extent from the rate of decomposition, and the product obtained in a vacuum is amorphous towards X-rays, but crystallises with the liberation of heat on subsequent heating. The formation of a product amorphous towards X-rays on dehydration under severe conditions is fairly common, and is not observed only in substances for which the lattice remains unchanged on the removal of water, for example zeolites, or when rearrangement of the structure takes place very rapidly. In our view, this is one of the chief factors preventing the fruitful application of thermodynamic and kinetic methods to the study of dehydration, since it leads to the production of such anomalous effects as the Smith–Topley effect in macrokinetics [170] or the departure of the temperature dependence of the vapour pressure from the logarithmic law for static measurements [183]. The excess of energy of the disordered phase for various substances varies in the range 3–7 kcal mole^{-1}. It is suggested that increase in the vapour pressure of water in the gas decreases the surface energy of the amorphous phase as a consequence of adsorption, and facilitates the formation of crystallisation nuclei. The residual water of intermediate hydrates or the "anhydrous" final products stabilises the disordered state, however. This is indicated, in particular, by the fact that in a number of instances [184-186] the temperature of removal of the last traces of water coincides with the temperature of the start of crystallisation of the reaction product. In condensed phosphates, the last few tenths of a percent of terminal hydroxyl groups are held extremely firmly [187] and are not removed completely in one month at 800°, preventing further polymerisation of the phosphates or their conversion into products with a ring structure.

Moreover, the kinetic characteristics of dehydration are influenced to a considerable extent by the degree of perfection of the crystals and the presence of macro- and micro-defects on their surface. Thus the rate of propagation of the reaction zone is different for the external surface and for a freshly exposed surface of a single crystal [188].

The above brief list of the most important characteristic features of dehydration demonstrates the sensitivity of these reactions to a great variety of factors, which makes it difficult to compare the thermal stabilities even for hydrates of the same type. For the same reasons, the discussion of the problems of predicting the direction of dehydration reactions on the basis of an analysis of the state of water in the original hydrate may lead to pessimistic conclusions, particularly in relation to the kinetic parameters of the process. A large number of results show that the number of stages in the reaction very seldom coincides with the number of kinds of water in the original hydrate. The chemistry of dehydration can be predicted

fairly unambiguously for hydrated zeolites and to a lesser extent for hydrates in which the water is not present in the coordination sphere of the cation. In the decomposition of aquo-complexes, however, the direction of the change in the structure of the coordination polyhedron of the metal is almost always unknown, so that the possible composition of the dehydration product also remains indefinite. The rearrangement of the structure on the formation of an intermediate hydrate also leads to a change in the initial state of the water and this evidently casts doubt on the method sometimes used to estimate the number of forms of water in a hydrate from the number of stages in its dehydration. In these instances, water fractions which are physically completely identical are removed in stages; this is also observed in systems with low hydrate numbers [189]. This provides evidence that the disordered phases formed in the dehydration have a microcrystalline structure, since otherwise we should not expect the formation of stable intermediate hydrates with a definite composition during dehydration.

An all-round approach to the analysis of the state of water in hydrates, however, makes it possible to explain most of the observed characteristic features of dehydration, and in a number of instances to predict their development. This applies particularly to the dehydration of hydrates in which the types of water differ sharply, for example many heptahydrates, for which the water molecule which is not present in the coordination sphere of the metal is removed first [180,190]. In the complex diphosphatoaluminate anion [191], four of the ten water molecules are coordinated to the metal and six are joined to phosphate groups, and in accordance with this, six water molecules are removed in the first stage of the dehydration.

From a large number of observations, albeit often only qualitative, it follows that dehydration is reversible only in its initial stages; the removal of the last water molecules is generally difficult and is most frequently irreversible. This irreversibility is usually attributed to kinetic factors, but some results indicate that in many instances it is due to irreversible changes in the salt, undergone in the dehydration of the original hydrate. Processes involving hydrolysis by water of crystallisation are familiar for various halogen systems and some nitrates [192-195]. A characteristic feature of these reactions is that the reactivity of the water of crystallisation does not show any clearly defined specific features, since hydrolytic decomposition of the anhydrous salts under the influence of water vapour is possible at the same temperatures. In accordance with this, the extent to which these reactions take place depends on the vapour pressure of water and the corresponding hydrogen halide over the substance undergoing dehydration.

In many instances, however, extensive dehydration is accompanied by changes in the substance which do not take place or which are even thermodynamically unlikely under the given conditions in the reaction of the anhydrous compound with water. It is not always possible to obtain an anhydrous salt with stoichiometric composition by dehydrating its hydrate. Qualitative information is available on the decomposition of the complex oxo-anion in the dehydration of carbonates [196], selenites [197,198], various sulphates [199-201], oxalates [202,203], and acetates [204]. These results were obtained for substances in which decomposition of the anion leads to the formation of volatile products, so that the simplest thermogravimetric methods can be used to establish that the process takes place. The study of the state of the solid dehydration product indicates that this phenomenon is much more widespread.

Our ideas on the dehydration of phosphates have altered radically in literally the last five years. The use of infrared spectroscopy [116,205,206], chromatography [207,208], and NMR [209] for the analysis of the solid phase has established that the extensive dehydration of both acidic and normal phosphates leads to extensive changes in the anion with the production of a mixture of condensed phosphates in the solid phase while the overall composition of the product remains constant. The final formation of crystalline ortho-, pyro-, or metaphosphates with increase in temperature results from secondary processes involving the reaction of oxides with higher phosphates.

The extent to which the anion decomposes may be different, but a large number of results indicate it is constant for a given substance and is almost independent of the conditions of the reaction, particularly the external water vapour pressure. Thus as in the case of metal halides, the theories of ordinary hydrolysis are evidently not applicable to these systems.

Mechanism of Dehydration of Crystal Hydrates

The widely encountered theories of the development of the reaction zone and the mechanism of thermal dissociation do not explain the above characteristic features of the extensive dehydration of solid inorganic crystal hydrates. They can be discussed from the viewpoint of the theories, examined in the previous section, of a unique "pre-dissociation" state of water in many lower hydrates. According to this, the first stage of this intracrystalline hydrolysis should be the transfer of the hydrogen of the water to the anion and the formation and possibly the stabilisation of acidic and basic groups in the substance on heating. In fact, these groups have been detected at definite stages of the dehydration in, for example, the dehydration of magnesium sulphate [200] or thorium oxalate [203]. Experimental data on the possibility of reorientation and rotation of water molecules, the high mobility of protons in solids, and the low height of the potential barrier for the migration of a proton along an H-bond makes this conversion extremely probable. When an acid salt is dehydrated, this process may lead to the formation of appreciable quantities of free acid in the substance [208]. Thus up to 15% of free phosphoric acid has been detected in the dehydration products in separate stages of the dehydration of calcium [206] and strontium [208] hydrogen phosphates. These results indicate that the formation of linear and cyclic polyphosphates is a secondary process in the dehydration of orthophosphates.

Theories of the energetics of hydrated compounds were used by Dombrovskii [210-213] to provide a qualitative explanation for various kinetic features of dehydration. The increase in the reaction rate on the addition of proton-donating substances and its decrease by proton acceptors indicate that dehydration involves proton transfer and not electron transfer, and results from the migration of protons in the lattice and on the surface of the crystal. The reversible decrease in the intensity of ν_{OH} with increase in temperature for a number of hydrates is also related to proton delocalisation, and the activation energy for the transfer of the proton to the conductivity zone has been estimated [214] as 2 kcal mole^{-1}. Increase in temperature leads to an increase in the mobility of the water molecule [215,216] and in the concentration of free protons in the lattice; this is accompanied by an increase in the proton conductivity when the substance is heated below its decomposition temperature [217].

The subsequent stages of the dehydration lead to the separation of metal oxides and the decomposition products of the corresponding ion in the gaseous or solid states; the temperatures of this decomposition of the anion may in a number of instances be lower by hundreds of degrees than the decomposition temperature of the anhydrous substance. The concentration of metal oxide in excess may reach several percent, so that care must be taken in the use of dehydration for preparative purposes, for example to obtain anhydrous substances and to determine their thermodynamic functions, particularly if allowance is made for the fact that on further heating, the oxides may react with the normal salt to form basic compounds.

If the anhydrous salt is not sufficiently stable to heat, it is impossible to distinguish processes of extensive dehydration and dissociation. This is due primarily to the lability of the disordered dehydration products. The water-containing formations, amorphous towards X-rays, are characterised by high proton mobility even at room temperature [209]. Thus on heating, partial dehydration is accompanied by fairly rapid rearrangement of the solid phase into a new quasi-stable state with a higher thermal stability than the original state. If allowance is made for the fact that the residual water stabilises the state amorphous towards X-rays, this continuous series of changes leads to the production of a dehydration temperature range which can extend to extremely high temperatures (700 to 800°) for compounds stable to heat. This scheme is confirmed by the extremely rapid decrease in the rate of dehydration in the final stages and by the temperature dependence of the degree of dehydration [218]. As expected, the temperature coefficient of the reaction rate corresponds to the temperature coefficient of diffusion in the solid, and this casts doubt on the commonly encountered suggestion that this course of the process is due to diffusion restriction of the removal of the gaseous product. The temperature dependence of the vapour pressure is not logarithmic, however, but is close to linear; this also is not contradictory to the scheme discussed.

The estimation of the relative probability of this "intracrystalline" hydrolysis of a salt can be based on a comparison of the extents of the influence of the cation and anion on the water. In actual fact, almost all known examples of the partial decomposition or rearrangement of a complex oxo-anion on dehydration involve substances containing an anion with clearly defined proton-acceptor properties and a strongly polarising electron-accepting cation. The substances for which the temperature ranges of dehydration and subsequent dissociation of the anhydrous salt are fairly clearly distinguished are chiefly the phosphates, selenites, and tellurites of transition and light metals forming multiply-charged cations. The relative extent of this decomposition of the anion changes qualitatively in the same order as the degree of distortion of the water molecule in the hydrate. For example, in the dehydration of normal zinc phosphate [206], almost no production of poly-forms is observed, whereas they are observed in appreciable quantities for the analogous compounds of cobalt, nickel, and copper.

The possibility that reactions of this kind also take place with substances which bind water less strongly cannot be neglected, however. For example, the rate of dehydration of beryllium sulphate tetrahydrate is influenced considerably by the presence of sulphuric acid on the surface of the crystal, although the decomposition takes place according to the stoichiometric equation [219].

The introduction of theories of the change in the state of water under the influence of only the cation and anion provides a qualitative explanation for the nature of the experimentally observed effects. For quantitative conclusions this approximation in a number of instances is insufficient, and it becomes necessary to make allowance for the influence of energetically weaker interactions on the water. For transition metal salts these may be interactions of the ferromagnetic or antiferromagnetic type between the cations, leading to some rearrangement of the electronic structure of the aquo-polyhedron. Thus in the dehydration of $CuSeO_3.\frac{2}{3}H_2O$, every sixth SeO_3^{2-} anion is decomposed, with the liberation of selenium dioxide into the gaseous phase [197]. The EPR spectra show that every sixth copper ion remains relatively isolated in this hydrate [220], and the rest take part in exchange interactions of the antiferromagnetic type, as confirmed by measurement of the temperature dependence of the magnetic susceptibility. The participation of the copper ions in exchange interactions leads to a redistribution of the electron density with a decrease in the strength of the M—O bond and a corresponding decrease in the energy of the H-bond formed by the water molecules coordinated to these ions. A water molecule joined to an isolated copper ion is therefore deformed to a greater extent, and this leads to decomposition of the anion on dehydration, by the mechanism examined above. The difference in the energies of the hydrogen bonds formed by the two types of water, determined by infrared spectroscopy, is ~1.2 kcal $mole^{-1}$, in good agreement with the energy of the magnetic interactions in di- and polynuclear complexes of copper with anomalous magnetic properties. The relationship between the effective magnetic moment and the frequency of the νCuO vibrations [221] confirms that weak interactions have a significant influence on the thermal dissociation of the substances.

The material examined leads to the conclusion that many characteristic features of thermal dehydration are determined by the state of the water in the lattice of the inorganic hydrate. The relative probability of decomposition of a complex oxo-anion can be estimated from data on the degree of distortion of the water molecules under the influence of the environment. The extent of this distortion is determined by the strength of the interaction of the water molecules with the cation and anion, and depends on the polarising and electron-acceptor properties of the cation and the proton-acceptor power of the anion.

The mechanism of these processes can be explained on the basis of theories of the dynamic nature of hydrogen bonding and the partial delocalisation of the protons when the hydrate is heated.

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