

Reviews

Proton mobility in hydrates of inorganic acids and acid salts

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Published data on the mechanisms of hydrogen ion transport in solids and aqueous solutions are described systematically, including defect formation, rotational mobility of proton-containing groups, proton hopping along a hydrogen bond, proton translational mobility, and proton conduction. Resorting to the authors' theoretical results and published data, the main criteria for the selection of systems possessing high proton mobility are formulated.

Key words: proton transport, hydrates, solid, proton hydration, rotational mobility, proton conductivity.

Introduction

Proton transport in condensed phases is of prime importance for the occurrence of many chemical, physical, and biological processes. Among them, a series of diffusion-controlled reactions including ion exchange can be distinguished.^{1–4} The phenomenon of proton conductivity⁵ and many life sustenance processes in living organisms and plants belong to the same class.^{6–8} Proton conductors are widely used in sensory units, fuel cells, steam electrolyzers, and power sources.^{5,9,10} The nature of proton transport in biological systems can be clarified only on the basis of thematic investigation of the diffusion processes in solids.^{7,8,11,12} The acquisition of new experimental results stimulates the development of new approaches to the interpretation of specific features of proton transport. Currently, an interesting prob-

lem is to elucidate the reasons for the abnormally high proton conductivity values observed in solutions of acids and bases. This phenomenon cannot be interpreted in terms of the generally accepted theories and can be explained only resorting to the views on the cooperative movement of protons in the $\text{H}(\text{H}_2\text{O})_n^+$ clusters.^{13–16}

The high practical significance of proton conductors stipulated the extensive quest for these materials. Since a proton, like an electron, is an elementary particle characterized by an extremely small radius (about 10^{-7} Å), these studies were expected to result in the synthesis of a large number of compounds with a proton conductivity as high as that observed for electrons. However, the researchers working in this field were faced with substantial problems. Unlike an electron for which the relatively free migration in condensed materials is ensured by the repulsion from the electron shells of the atoms or ions

that form the substance, a proton is efficiently attracted to the electron shells, which substantially hampers the transfer. In this respect, the situation is even worse than for other cations having their own electron shells, which decrease the efficiency of this interaction. Therefore, it is reasonable to assume that the mechanism of proton transport in condensed media differs dramatically from the mechanism found for electrons or other ions.

After Bernal and Fowler's publication,¹⁷ it has been assumed that the proton migration proceeds through successive proton jumps and rotation of proton-containing groups. It has long been considered that molecular rotation, at least, in liquids, occurs at very high rates and, therefore, the proton jumps play the predominant role in transport processes. Therefore, most studies have dealt with proton hopping along the sequence of H-bonds. However, a number of results indicate that the rotation of molecules and ions is equally important for the transport (see, for example, Refs. 14 and 18). The chemical nature and the ratio of proton-accepting abilities of the electronegative atoms involved in the transport are significant for both of the above-mentioned processes. Finally, the presence of a rather high concentration of defects, which ensure the transport, is also an important factor.

Most of low-temperature proton conductors are hydrates of acid and acid salts. An increase in the number of water molecules in the compound results in an increase in the proton conductivity,^{19,20} which approaches, in the limit, the conductivity of aqueous solutions. Therefore, it is reasonable to assume that the proton mobility in solid acid hydrates is of the same nature as that in their aqueous solutions, the only difference being a higher concentration of acid protons and a lower intensity of atom vibrations in solids.

The main goal of the present review is to discuss the nature of high proton mobility in solid hydrates of acids and acid salts at low temperatures based on published data and some original results and to identify conditions needed for high proton mobility to be manifested. The key mechanisms of the formation of proton defects and various types of mobility in these class of compounds are considered successively. In conclusion, we attempted to give a prognosis of the compositions of compounds in which fast proton transport is highly probable.

Defect formation

The migration of ions in a solid is possible only through transport of structural defects, which are represented most often by vacancies or interstices.² The rate of transport processes is determined by the product of the defect concentration by the defect mobility. Therefore, the understanding of defect formation processes is as important for creation of an integrated view on the transport phenomena as the description of the defect

migration mechanism. Indeed, the low conductivities of semiconductors and liquid water are due to low concentrations of defect centers in these materials. The addition of electron donors or acceptors to semiconductors or strong acids or bases to aqueous solutions entails an essential increase in the conductivity due to defect formation (e^- , h^+ or H_3O^+ , OH^-). The chemistry of defects also plays a key role in the ion transport processes in solid electrolytes. A high concentration of defects is an important feature of the so-called superionic conductors. Now we consider the most popular mechanisms of defect formation in solids.^{4,21}

A. Equilibrium defect formation due to thermal disorder of atoms, which proceeds strictly according to thermodynamic laws. The formation of this type of defects contributes to the increase in the conductivity of non-metallic substances at elevated temperatures.

B. Formation of non-equilibrium defects on fast cooling (quenching) of substances. For example, in perovskites, the formation of these defects is related to retardation of oxygen sorption/desorption in a specified temperature range. Defects of this type are often characterized by low mobility, and they do not result in high ionic conductivity.

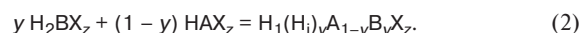
C. Formation of interstitial (admixture) defects upon chemical treatment of compounds. The most typical procedure is doping of ionic crystals with compounds of elements with a different valence. The processes related to charge compensation may give rise to defects of various types, depending on the nature of the doping reagent.

D. Formation of defects at the solid—solid or solid—liquid interface. For example, the contact with an inert highly dispersed phase can induce a substantial increase in the ionic conductivity of systems containing substances with a low concentration of intrinsic defects.^{22–24}

E. Defect formation on the surface of particles due to uncompensated chemical bonds.^{25,26}

F. Defects formed during mechanical treatment of substances deserve special attention.^{27,28} This mechanism is the most important for a broad range of mechanochemical processes.^{1,29}

Defect-formation mechanisms *A* and *E* are found most often among proton conductors. However, the former can hardly play a substantial role in most crystal hydrates of acids and acid salts, because these compounds are stable over relatively narrow temperature ranges. Doping (*C*) is often used to increase the conductivity of solid electrolytes. For example, proton defects may arise according to the reactions



As a consequence, the matrix becomes enriched in proton vacancies (V_H^+) or interstices (H_i), respectively. This method is often used to create a specified concentration of defects in solids. However, it is used much more rarely for low-temperature proton-conducting electrolytes, apparently, due to relatively low solubility of the heterovalent impurities in inorganic crystal hydrates.

The next, perhaps, the most promising method for increasing the ionic conductivity includes preparation of composite electrolytes by the addition a highly dispersed phase (I). The intense sorption processes that occur at the interfaces within a rather narrow, $\sim 1\ \mu\text{m}$ -thick Debye layer give rise to a high concentration of defects. This entails an increase in the ionic conductivity of the system as a whole.^{22–24} When the content of the inert phase is low, its particles are isolated from each other, and the highly conductive layer formed at the interface ensures an efficient contact between the crystals of the ionic salt. This leads to a substantial increase in the conductivity, which is virtually proportional to the additive concentration. Large amounts of the inert phase block up the ionic crystals. This results in a decrease in the system conductivity. Therefore, the conductivity of composite electrolytes, as a rule, passes through a maximum when the content of the highly dispersed oxide phase is 20 to 40%.⁴

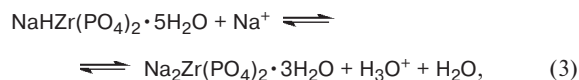
Numerous attempts have been made to increase the proton conductivity of a well-known solid proton-conducting electrolyte, zirconium hydrogen phosphate monohydrate (α -ZrP), by introduction of inert additives. The early attempts failed. For example, no marked increase in the conductivity has been found in α -ZrP composites with alumina or silica gel.^{30,31} However, later, a 5 to 10-fold increase in the conductivity was found for the same systems at $\sim 20\ \text{mol.}\%$ content of the oxide phase.³² The main reason for the relatively slight increase in the conductivity in these systems, was, apparently, the use of finely dispersed α -ZrP with high surface conductivity. Recently,³³ we demonstrated the possibility of attaining a much greater increase in the conductivity of crystalline α -ZrP upon chemical modification of its surface by a thin layer of an exchange product. The content of the doping phase that ensured the maximum effect (1–5%)³³ was much lower than in most studies dealing with the ion conductivity of composite materials.

The synthesis of composite electrolytes in the $\text{MHSO}_4\text{--SiO}_2$ and $\text{MHSO}_4\text{--TiO}_2$ systems ($M = \text{K}^+, \text{Rb}^+, \text{Cs}^+$) has been studied.^{34–39} The conductivity of the cesium system increases by 2.5 orders of magnitude with respect to the low-temperature CsHSO_4 phase. The composites are characterized not only by reduced melting points but also by reduced enthalpies of the superionic phase transition.^{34,35} This phenomenon can be interpreted using the theory of the order–disorder phase transitions, according to which the defects present in a solid facilitate transition of the neighboring atoms or ions from

the ground positions to excited states. A defect concentration of the order of several percent can be critical for the transition of a substance to the superionic state. Owing to the high ion mobility near the particle surface, phase transition takes place also in deeper layers. Thus, the formation of a highly defective region at the interface can affect significantly the properties of the whole ionic crystal.⁴

The most pronounced increase in the mobility in ionic compounds can be attained by increasing the sorption ability of the doping phase contacting with them (with respect to any of the ions contained in these compounds) and by ensuring the maximum surface area of phase contact. For instance, a substantial increase in the mobility can be expected for the contact between ionic compounds and solutions of compounds that exhibit considerable affinity to one of the ions contained in the material. In the case of proton-conducting electrolytes, this role can be performed by solutions of acids or alkalis.

Let us consider the results of our study^{40–45} dealing with the ion exchange kinetics in the $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ – NaCl – NaOH system. In the second stage of the exchange, which follows the scheme



the process rate is controlled by proton diffusion through the layer of the $\text{Na}_2\text{Zr}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ product formed. The diffusion coefficient of protons is determined by the concentration of defects in a solid. This concentration, in turn, depends on the solution pH and on the nature of the anion in the supporting electrolyte^{42,43} (Fig. 1). The apparent diffusion coefficient calculated from experimental data increases by three orders of magnitude as the pH varies in the range of 6.5–10.5, which is due to the formation of proton vacancies (OH^- ions) in $\text{Na}_2\text{Zr}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$. As the pH varies from 6.5 to 5.5,

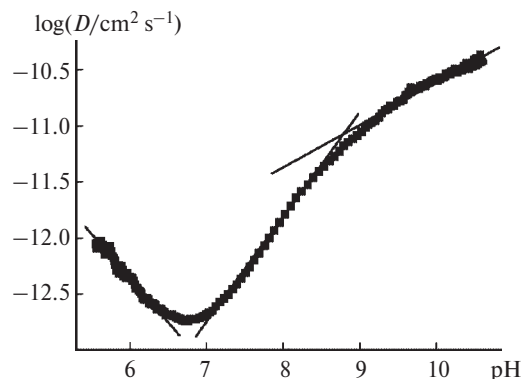


Fig. 1. Diffusion coefficient (D) of hydrogen ions in $\text{Na}_2\text{Zr}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ vs. the solution pH during the titration of zirconium hydrogen phosphate.

the diffusion coefficient also increases due to the formation of proton interstices (H_3O^+).^{41–43} The magnitude of this effect markedly exceeds that observed for the interaction of solid phases.⁴⁵ This phenomenon resembles the increase in the proton conductivity of liquid water induced by the addition of acids or bases.

Mechanism *E* is encountered most often in highly dispersed systems. It is similar in essence to the phenomena at an interface where one phase is the atmosphere, in which the measurements are carried out. The sorption processes taking place on the material surface are somewhat less efficient. However, by an appreciable decrease in the particle size, in this case, too, a noticeable effect can be attained. After grinding of the substance crystals down to a size smaller than twice the Debye band width, the conductivity increases throughout the whole bulk of the crystals.²⁶ Therefore, when investigating finely dispersed materials, researchers deal most often with the surface component of the conductivity. This value dictates the properties of a large number of solid-state proton conductors, among which globular hydrates should be specially noted.^{19,20} Hydroxides of polyvalent elements represent a typical example of these materials.⁴⁶ The nucleus of particles forming these materials resembles in composition the corresponding oxide, and the surface contains a large number of OH groups, water molecules, and, in some cases, anions captured from the solution. The OH groups dissociate in conformity with the acidic or basic nature to give a highly mobile thin film of an acidic or alkaline solution on the surface of globules. Phenomena of this type seem also to take place in the conductive channels of ion exchange membranes.⁴⁷ Typical features of these systems include a sharp bent in the temperature dependence of the con-

ductivity plotted in the Arrhenius coordinates²⁶ and the variation of the conductivity with the degree of dispersion of the material.⁴⁸

Proton-containing compounds, unlike other substances, are characterized by one more, specific type of defectiveness, namely, orientational disorder. It is due to the fact that a proton is always bound to some electronegative atom by a valence bond and, most often, it is linked by H-bond to a close neighbor. The dependence of the potential energy of these systems on the position of the proton on the H-bond line normally has two minima corresponding to proton localization at a particular O atom. When the bond is formed, the proton occupies only one of these minima (Fig. 2, *a*). However, according to Bjerrum, system disorder can give rise to two types of orientation defects. A hydrogen bond without protons (Fig. 2, *b*) is referred to as L-defect, while an H-bond with protons in both minima (Fig. 2, *c*) is called D-defect. In ice, these defects can arise due to rotation of water molecules. Analysis of the structures of a large number of inorganic hydrates of acids and acid salts⁴⁹ shows the presence of numerous Bjerrum L-defects (short O—O contacts without a proton). However, we found only one example of an H-bond with two protons (the H_5O_2^+ ion in $\text{H}_{3.33}[\text{Fe}(\text{CN})_6] \cdot 2.66\text{H}_2\text{O}$).⁵⁰ Apparently, due to the high energy of formation of Bjerrum D-defects related to the very short distance between two protons, this bond is seldom encountered.

Ab initio calculations (6G-316* basis set) carried out using the Hyper.Chem. package, release 4.0 for Windows (Hyper Cube, Inc., 1994) show that the energy of D-defect formation for an H-bond with $R_{\text{O—O}} = 2.98 \text{ \AA}$ is 3 times as high as the energy of L-defect formation. This difference becomes even more evident for $R_{\text{O—O}} = 2.8 \text{ \AA}$

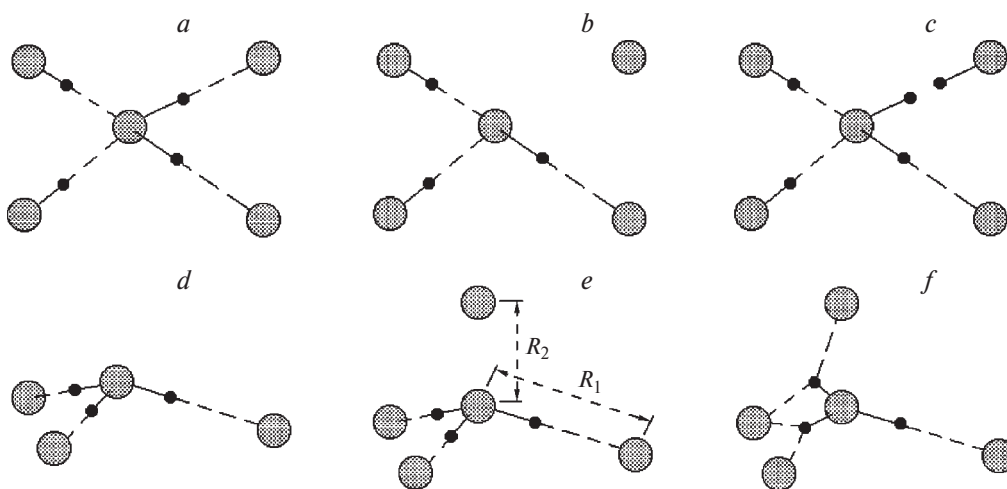


Fig. 2. Schemes of H-bonds in water (*a*); formation of the Bjerrum L- (*b*) and D-defects (*c*) in the ice structure, H-bonds of the oxonium ion (*d*), and the oxonium ion with an additional H-bond (*e*), and the scheme of formation of a new H-bond during the group rotation of H—OH_2^+ (*f*); R_1 is the length of the H-bond involved in the proton transport; R_2 is the distance to the nearest O atom not involved in the H-bond formation.

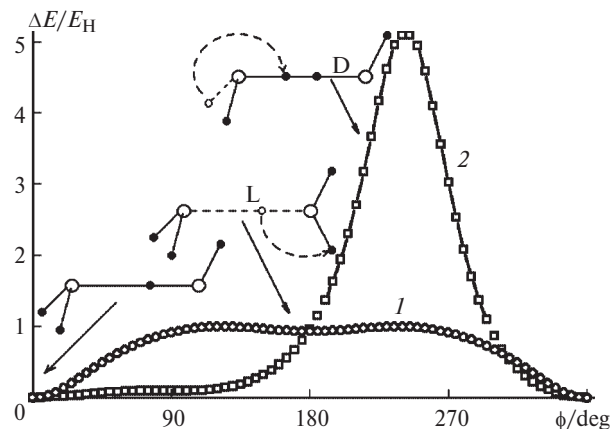


Fig. 3. Relative change in the energy of the HOH—OH₂ system during the rotation of water molecules through the formation of Bjerrum L- (1) and D-defects (2).

(the energy difference is ~5 times, Fig. 3). The H-bond energy halves when the bond axis deviates from the line connecting the centers of atoms by an angle of 45°, decreases 3-fold when the angle is 60°, and for rotation angles of ~90°, the energy decreases almost to zero (see Fig. 3).

Rotation of proton-containing groups

Molecular rotation is known to be a necessary step providing proton transport in solids.^{14,15,18,20} The transport requires that all the H-bonds formed by a water molecule be cleaved; the energy of these bonds can be estimated on the basis of interatomic distances or IR-spectroscopy data. The minimum number of H-bonds that need to be cleaved for re-orientation of an H₂O molecule occurring in a tetrahedral environment is three. This is possible if an H₂O molecule rotates relative to one H-bond (a threefold axis in the ice structure, see Fig. 2, a). However, this mode of rotation should involve intermediate formation of Bjerrum D-defects (see Fig. 2, c), which are characterized, as shown previously, by high energies. Therefore, rotation of H₂O molecules around the bisector of the H—O—H angle is the most typical situation. This pattern requires cleavage of all the four H-bonds.

As the number of bonds formed by an H₂O molecule decreases, the rotational mobility of the molecule increases. Let us compare the mobility of H₂O molecules in magnesium and lithium perchlorate hydrates, Mg(ClO₄)₂·6H₂O and LiClO₄·3H₂O. According to structural data,^{51,52} the water molecules in LiClO₄·3H₂O are coordinated by two cations, whereas in Mg(ClO₄)₂·6H₂O, they are coordinated by only one cation. Despite the fact that the H-bonds and the overall interaction of the water O atom with the metal in Mg(ClO₄)₂·6H₂O is stronger than that in LiClO₄·3H₂O,

re-orientation of H₂O molecules relative to the Mg—O direction takes place at temperatures of >150 K. The mobility of water in LiClO₄·3H₂O does not show itself up to the dehydration temperature. Thus, a decrease in the number of bonds formed by H₂O molecules with respect to that in the most prevalent tetrahedral coordination entails a higher mobility of these molecules, even with some strengthening of the remaining bonds.⁵³

It has been shown previously¹⁴ that an increase in the concentration of oxonium ions in aqueous solutions decreases the mobility of H₂O molecules due to an increase in the energy of H-bonds. This conclusion is consistent with the results^{54,55} of calculation of the bond energies in the H(H₂O)_n⁺ ions. The energy of the central H-bond in H₅O₂⁺ amounts to ~150 kJ mol⁻¹, which is close to the energy of a typical chemical bond. An oxonium ion can form three strong H-bonds, each with an energy of 80–150 kJ mol⁻¹.^{55,56} This value exceeds substantially the corresponding parameters for ice or liquid water (15–25 kJ mol⁻¹).

When investigating the mobility of proton-containing groups in a solid by NMR, we also found^{49,57} that the formation of strong H-bonds in systems containing a hydrated proton markedly decreases the rotational mobility of H(H₂O)_n⁺ fragments. Thus, oxonium ions possess the highest mobility. In crystal hydrates containing H₅O₂⁺ ions, only rotation of the H₂O molecules with respect to the central H-bonds takes place. In the case of hydrates with higher degrees of hydration, no rotational mobility is normally observed up to the melting points. Nevertheless, the rotational mobility of H(H₂O)_n⁺ ions in solid hydrates of acids or acid salts is normally higher than that of H₂O molecules in normal solid salt hydrates.⁵⁷ Note that, contrary to the previous data,¹⁴ the addition of strong acids to aqueous solutions was found to increase the rotational mobility in the system.⁵⁸

One reason for the increase in the rotational mobility of the H(H₂O)_n⁺ ions in solids is low proton-accepting ability of the anions contained in them. Indeed, a theoretical possibility of proton hydration in solids appears only in the event that the proton affinity of the anion is lower than that of H₂O molecules.⁴⁹ This, in turn, results in the formation of a weak H(H₂O)_n⁺—anion H-bonds. Another (equally important) reason is the fact that proton hydrate systems always incorporate a number of O atoms with uncompleted octahedral environments, which are involved in the formation of only three H-bonds (see Fig. 2, d). Thus they acquire the ability to rotate about one H-bond with cleavage of the two weaker bonds.

The positive charge of the H₅O₂⁺ ions does not allow them to serve as acceptors of additional H-bonds. Therefore, the O atoms of these ions participate in the formation of three H-bonds located on one side of the O atom (see Fig. 2, d), the average angle between the bonds

being $\sim 112^\circ$.⁴⁹ The asymmetric H_3O^+ fragment of the diaquated hydrogen ion is a dipole with a negative charge on the O atom. Since the interaction of a dipole with a charged species is attenuated with an increase in the distance between them much faster ($\sim 1/r^3$) than the interaction between two charged species ($\sim 1/r$), the placement of an additional O atom on the other side of the H-bonds (see Fig. 2, *e*) is expected to result in a decrease in the system energy for O—O distances greater than 3 Å. When analyzing structural data for a large number of hydrates of acids and acid salts, we found these additional electronegative atoms virtually in every compound subjected to analysis.⁵⁹ This implies that these structures contain initially the Bjerrum L-defects. The rotation of the OH_2 fragment in the H_5O_2^+ ion around the short H-bond enables the formation of two new H-bonds for rotation angles of ~ 120 and 240° . According to published data,⁵⁷ this also increases the rotational mobility in the given system.

In most of solid hydrates incorporating the H_7O_3^+ ion, one stronger H-bond can also be distinguished. Therefore, these compounds can be regarded as some approximation as H_5O_2^+ hydrates. The short H-bonds in solid hydrates of this type are asymmetric ($\text{H}_3\text{O}^+ - \text{OH}_2$) and are somewhat weaker than those in isolated H_5O_2^+ ions. Therefore, in addition to the rotation of the OH_2 fragments relative to the short H-bond considered previously, the possibility of rotation of oxonium ions relative to the C_3 axis may also appear.

The activation energy for the rotation of proton-containing groups has been traditionally interpreted as the energy of H-bond cleavage, which was estimated on the basis of the length of the O—O contacts or using the data of IR spectroscopy.⁶⁰ However, a systematic NMR study of the rotation of water molecules and H_3O^+ and H_5O_2^+ ions in the solid hydrates of strong inorganic acids and acid salts showed⁵⁷ that the activation energy for rota-

Table 1. Rotation energy of the $\text{H}(\text{H}_2\text{O})_n^+$ ions ($E_r/\text{kJ mol}^{-1}$) calculated in our work (I) and determined from ^1H NMR data (II)

Compound	Rotating group	$R_{\text{O}-\text{O}}^*$ /Å	E_r		Ref.
			I	II	
$\text{H}_3\text{OV}(\text{SO}_4)_2$	H_3O^+	2.80	23	22 ± 2	57
$\text{H}_3\text{OIn}(\text{SO}_4)_2$	H_3O^+	2.87	18	18 ± 2	57
$\text{H}_5\text{O}_2\text{In}(\text{H}_2\text{O})_2(\text{SO}_4)_2$	$\text{H}-\text{OH}_2^+$	2.71	25	24 ± 2	57
$\text{H}_5\text{O}_2\text{Ta}(\text{PO}_4)_2$	$\text{H}-\text{OH}_2^+$	2.73	25	23 ± 2	61

* The average value for the outer H-bonds is given.

tion found experimentally is always lower than the energy of H-bond cleavage. Taking into account the earlier data concerning the change in the energy of H-bonds during the rotation of proton-containing groups (see Fig. 3), we suggested that this process occurs by cleavage of some H-bonds and formation of other H-bonds and passes *via* a transition (activated) state having so-called forked (bifurcated) H-bonds (see Fig. 2, *f*). This suggestion underlay a method for the calculation of the activation energy for the rotation of proton-containing groups.⁵⁶ The values thus obtained proved to be in quite satisfactory agreement with the experimental data for all the studied compounds (Table 1).

When analyzing the results of calculations of the activation energies for different models of rotation of the $\text{H}(\text{H}_2\text{O})_n^+$ ions in the ice ($R_{\text{O}-\text{O}} = 2.76$ Å) and liquid water ($R_{\text{O}-\text{O}} = 2.85$ Å) matrices (Table 2), one can easily see that the rotational mobility of all proton hydrates in an ice matrix should exceed the water mobility. When the H-bond length has increased to 2.85 Å, only the H_9O_4^+ ions are found to be somewhat less mobile. In the predominant mechanism, the $-\text{OH}_2$ fragments of the $\text{H}(\text{H}_2\text{O})_n^+$ ions rotate around short H-bonds. The rotational mobility of these ions decreases with an in-

Table 2. Calculated activation energies for the model rotation systems of the $\text{H}(\text{H}_2\text{O})_n^+$ ions in ice (I) and aqueous (II) matrices

Model group	Rotating group	$R_{\text{O}-\text{O}}^*/\text{Å}$		$E_r/\text{kJ mol}^{-1}$	
		I	II	I	II
H_2O	H_2O	4×2.76	4×2.85	62	47
H_3O^+	H_3O^+	3×2.76	3×2.85	33	24
H_5O_2^+	H_3O^+	$2.55 + 2 \times 2.76$	2×2.85	45	39
H_7O_3^+	H_3O^+	$2 \times 2.55 + 2.76$	$2 \times 2.55 + 2.85$	57	55
H_9O_4^+	H_3O^+	3×2.55	3×2.55	70	70
H_5O_2^+	$\text{H}-\text{OH}_2^+$	$2 \times 2.76 (+2.76)$	$2 \times 2.85 (+2.85)$	22	16
H_7O_3^+	$\text{H}-\text{OH}_2^+$	$2 \times 2.55 + 2.76 (+2.76)$	$2 \times 2.55 + 2.85 (+2.85)$	36	34
H_9O_4^+	$\text{H}-\text{OH}_2^+$	$3 \times 2.55 (+2.76)$	$3 \times 2.55 (+2.85)$	50	52

* The mean value for the H-bonds to be cleaved and the number of these bonds are given; the value in parentheses is the distance to the additional H-bond acceptor not involved in the H-bonding in the ground state of the ion.

crease in n , which is in line with NMR data.⁵⁷ The highest mobility is typical of water molecules acting as donors of only one strong H-bond with oxonium ions ($n = 2$ or 3). In the case of proton hydrates with $n \geq 4$, each water molecule forms, as a rule, four H-bonds, which are stronger than those in ice. The formation of these ions is typical of aqueous solutions. Since their rotational mobility is lower than that of H_2O molecules, the appearance of such ions should not induce an increase in the rotational mobility.

The cooperative nature of phenomena is significant for the rotational mobility.⁶² Indeed, an H_2O molecule that has passed into the isotropic rotation state should be regarded as a neutral spherical species rather than a dipole. This transition results in the cleavage of all H-bonds formed by this molecule, which facilitates the rotational mobility of the close neighbors. Their rotation induces the mobility of the next layer of adjacent molecules and, thus, of the system as a whole. Thus, some of H-bonds formed by water molecules and proton hydrates in $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$, in which the anion O atoms having a low proton-accepting ability act as donors, are very weak. The high rotational mobility of these fragments, which, in turn, function as acceptors of other H-bonds, propagates over the whole proton hydrate sublattice due to cooperative effect. Therefore, the transition to the highly mobile state takes place at low temperatures.⁵⁷

A similar transition to the mobile state at low temperatures has been reported for layers of H_2O molecules adsorbed on the surface of some inorganic compounds.²⁰ The soliton mechanism, which implies passage of a wave of mutually consistent re-orientations with a slight phase lag, appears to be inapplicable for explaining the high proton conductivity of this type of system. According to a model calculation, the activation energy for the concerted re-orientation of a chain of H_2O molecules rapidly increases with an increase in the number of molecules that participate simultaneously in such a motion. This is due to the fact that such re-orientation requires simultaneous cleavage or weakening of a number of bonds, which is associated with additional loss of energy.

Proton hopping along hydrogen bonds

The hops of a proton along the line of H-bonds is a key point in the proton transport. As for any other activation process, the frequency of hopping is determined by the pre-exponential factor (the frequency of stretching vibrations of the O—H bonds) and by the activation energy. The latter value can be found from the curve for the proton potential energy vs. its position on the H-bond line. As a first approximation, the activation energy of hopping is dictated by two factors, the distance between the proton donor (A—H) and acceptor (B) and the difference between their proton-accepting abilities, which

can be expressed in terms of the difference between the acid dissociation constants of the A—H and B—H groups (ΔpK) or as the difference between the energies of proton binding by A and B ($\Delta H \approx 2.3RT\Delta pK$).

In numerous works, the energy profiles of proton migration along the H-bonds have been calculated and correlations between the bond length and the activation energy of this process have been elucidated. In most of these works,^{63–65} calculations were carried out for the O—H—O H-bonds with equivalent O atoms. The results of our MNDO calculations⁵⁹ were consistent with the data obtained by other researchers;⁶⁵ however, both differ markedly from experimental values. In our opinion, this disagreement is due to vibrations of the O atoms of the O—H—O bonds. As a first approximation, according to estimates based on precision structural studies, the amplitude of these vibrations can reach several tenths of angstrom. Thus, for part of the time, the O atoms are separated by distances shorter than the equilibrium distance. At these instants, the frequency of proton hopping should increase, as indicated by the same calculations. Similarly, the activation energy for the cleavage of H-bonds in liquid water at room temperature is $\sim 5 \text{ kJ mol}^{-1}$, which is ~ 3.5 lower than the average energy of H-bonds in them.⁶⁶ Presumably, such bonds are mainly cleaved, on the contrary, at the instants when the O atoms are farthest removed from each other.¹⁶

The abnormally high proton mobility in the H_2O molecule has been interpreted^{13,67} by structural migration of H_9O_4^+ (H_5O_2^+) ions, which occurs due to local changes in the structure during thermal vibrations. Subsequently,^{68,69} quantum-molecular dynamics calculations were carried out for this model. According to the obtained data, transition from the proton hydrate based on the H_5O_2^+ ion (Fig. 4, *a*) to the H_9O_4^+ ion with three equivalent H-bonds (Fig. 4, *b*) occurs with a frequency of $\sim 10^{13} \text{ s}^{-1}$. Then a new hydrate based on H_5O_2^+ is produced (Fig. 4, *c*). Due to the necessity of a concerted rearrangement of a rather large structural fragment, the transition between the two outermost configurations proceeds an order of magnitude more slowly. In solids where the vibrational mobility of atoms and the hydration are moderate, compared to those in liquids, the efficiency of this mechanism and the polarizability of H-bonds are appreciably lower.⁷⁰ Apparently, the high frequency of proton hopping along the short H-bond and the vibrational disorder of hydrated systems are the main reasons for the fact that debates concerning the degree of proton hydration are held in the literature.^{56,71} Most of the obtained results attest that hydrated form of the diaquated hydrogen ion is the predominant species.^{49,56,69,71}

Thus, the correct value for the proton hopping frequency can be determined by averaging the calculated values over a broad range of interatomic distances, in conformity with the probability of their existence. Un-

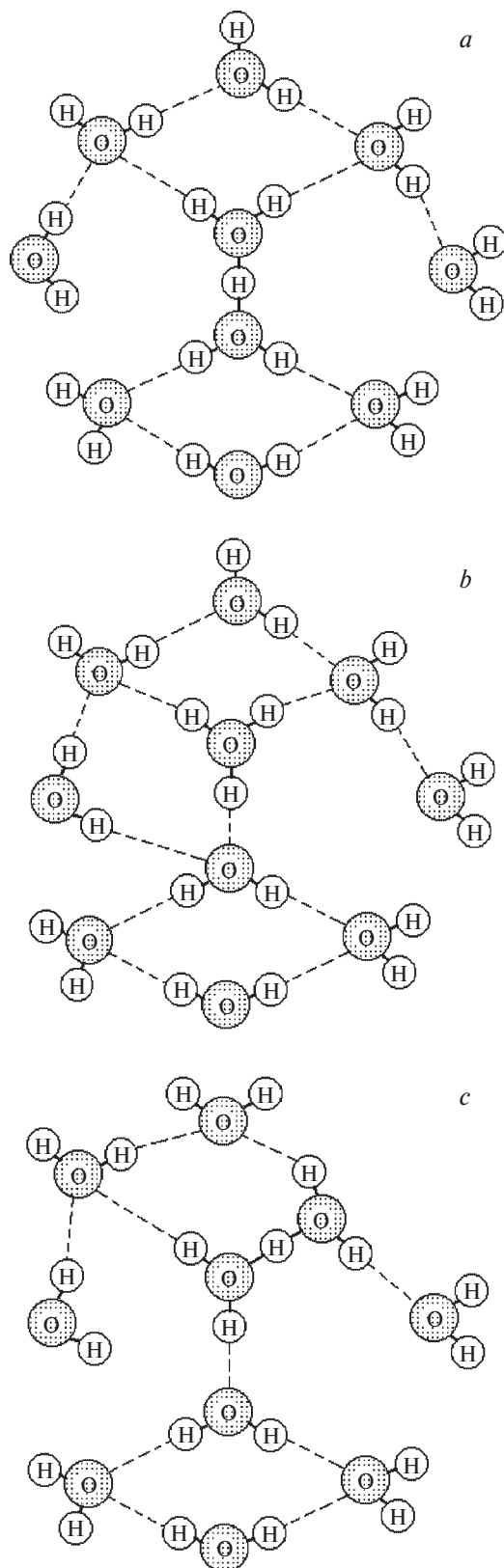


Fig. 4. Scheme of proton transport in aqueous solutions of acids: *a–c* are successive steps of the process.

fortunately, no reliable data on the probability density for the distribution of O atoms inside the ellipsoid of revolution can be found in the literature. The hopping activation energies estimated under the assumption of Boltzmann distribution of the O atoms over interatomic distances $p(R_{O-O}) = f(E)$ prove to be much closer to the values measured experimentally, although they are still overestimated. In addition, each real structure has its own amplitude and orientation of vibrations. When drawing an analogy between the proton hopping frequency and polarizability of H-bonds, one should take into account a number of other parameters that also affect the rate of transport. These include, in particular, the interaction of thermally initiated vibrations with phonons and polaritons⁷² and the influence⁷³ of the environment, first of all, the degree of hydration of the system.⁷⁴ In view of this, we used in model calculations a semi-empirical method for the estimation of the activation energy of proton hopping. This approach is based on the calculation of the activation energy of hopping using the difference between proton-accepting abilities of the H-bond donor and acceptor (ΔH) and the height of the potential barrier to a proton jump between a pair of equivalent O atoms determined by MNDO calculations (E_a).⁷⁵ The derived relation provides the activation energies of hopping close to experimental values. For small ΔH values, they are determined by the activation energy calculated for a system with $\Delta H = 0$, while for higher proton-accepting ability, they are dictated by the ΔH value.

The proton hopping and molecular rotation frequencies were calculated using the Arrhenius equation. For most of H-bonds, the pre-exponential factor for proton hopping is equal to the stretching frequency of the OH bonds and is close to 10^{14} s^{-1} .⁷⁵ This value somewhat decreases in the case of very short H-bonds whose formation hampers the rotation of proton-containing groups and prevents manifestation of the high proton mobility in the system.

Proton transport

Since proton transport can be described as a combination of rotations of proton-containing groups and proton jumps between them, the frequency of the overall process (ν_{tr}) can be found from the relation

$$1/\nu_{tr} = 1/\nu_r + 1/\nu_j, \quad (4)$$

where ν_r and ν_j are the frequencies of rotation of the proton-containing groups and of the proton jumps between them, respectively. The calculated activation energies and the frequencies of proton transport along the A–B...A–B chain are shown in Fig. 5. Due to restric-

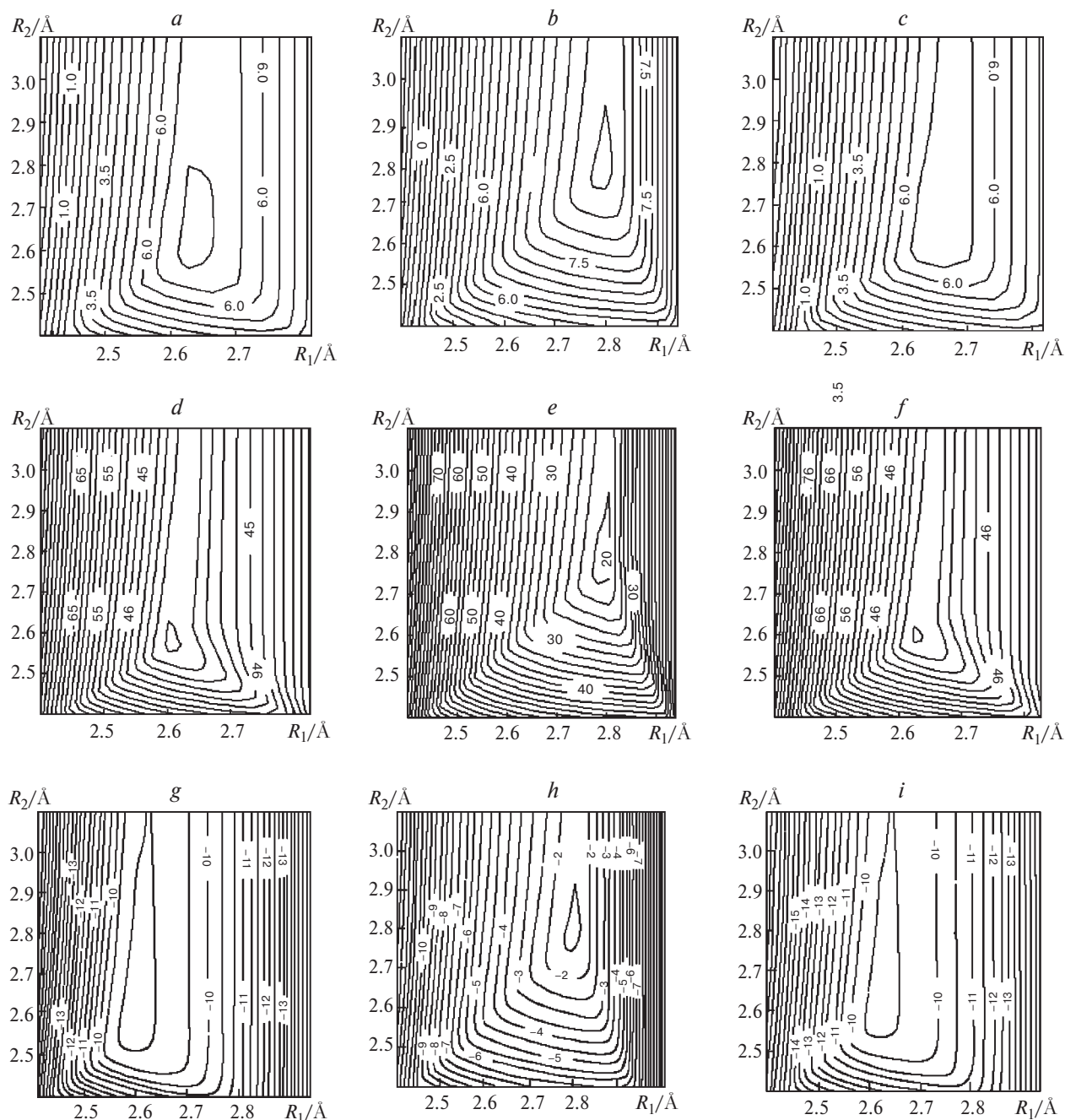


Fig. 5. Dependences of the logarithm of frequency (ν/cm^{-1}) (a–c), activation energy ($E_a/\text{kJ mol}^{-1}$) (d–f) of the proton transport, and logarithm of the conductivity ($\sigma/\text{S cm}^{-1}$) (g–i) of acid and acid salt hydrates vs. the lengths of H-bonds of the $\text{H}(\text{OH}_2)_n^+$ ions; ΔH (kJ mol^{-1}) = -45 (a, d, g), 0 (b, e, h), and 45 (c, f, i).

tions related to the choice of the coordinate frame, the abscissa represents the average length of H-bonds involved in the proton transfer (R_1), and the value laid off along the ordinate axis is the length of the excess H-bond (R_2) stimulating the rotational mobility of the proton-containing groups (see Fig. 2, e). The angle between the H-bonds for these groups was taken to be 114° , which is a typical value for oxonium ions.⁴⁹

The activation energy of the proton transport (see Fig. 5) has a minimum whose position on the abscissa shifts to the region corresponding to shorter H-bonds, as the magnitude of ΔH increases. The lowest activation energy ($\sim 19 \text{ kJ mol}^{-1}$) is found for $\Delta H = 0$ and $R_{\text{O} \cdots \text{O}} \approx 2.78 \text{ \AA}$. As was to be expected, the proton transport along short H-bonds is controlled by rotation of the $-\text{OH}_2$ fragments, while in the case of long bonds, it is

limited by proton hopping along the bonds. Note that the shift of the minimum activation energy of transport toward shorter H-bonds proceeds faster if the proton-accepting ability of the anion is lower than that of the H_2O molecule. This is due to lower pre-exponential factors for the rotation of proton-containing groups. In addition, high degrees of hydration are found for some compounds with a low proton-accepting ability of the anion.⁴⁹ Typical examples are heteropolyacid hydrates ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$). In this case, proton transport along a chain of H-bonds between H_2O molecules having the same proton-accepting ability without participation of the anion O atoms may prove to be preferred. The low proton-accepting ability of the anionic sublattice results in a lower activation energy for the rotation of proton-containing groups in these compounds (see above).

As noted above, the cooperative nature of proton transport plays an important role in this process. Besides the phenomena described above, the fact that the vibrational mobility induces inevitably weakening of some H-bonds and strengthening of some other bonds in the system deserves special attention. The situation is reversed in the opposite phase of vibrations. Whereas strengthening of H-bonds entails a decrease in the activation energy and acceleration of proton hopping, the weakening of bonds enhances the rotational mobility. These processes are thus separated in space. However, in the subsequent phase of vibrations, the transport process in each of the considered regions can be completed. The higher the structural disorder and the weaker the bonds formed there, the greater the amplitude of vibrations and the higher the rate of transfer. Therefore, it is not surprising that the maximum proton mobility is attained for aqueous solutions, for matrices of heteropolyacid hydrates, and for liquid layers sorbed on the surface of small solid particles. In these materials, an H-bond network optimal as regards the transport is combined with weakness of bonds, which results in a great vibration amplitude and in the highest efficiency of cooperative processes. The same reasons account for the low activation energy for the transport in aqueous solutions.

Similar cooperative phenomena have been considered for the crystals of the MXAO_4 , $\text{M}_3\text{X}(\text{AO}_4)_2$, and $\text{M}_5\text{X}_3(\text{AO}_4)_4$ families ($\text{M} = \text{NH}_4$, K, Rb, Cs; $\text{X} = \text{H}$, D; $\text{A} = \text{S}$, Se)⁷⁶ and for the KH_2PO_4 family.⁷⁷ Cooperative nature of proton transport has been noted for the small molecules of salts of polyfunctional organic acids,^{78,79} for chains of the acid— $(\text{H}_2\text{O})_n$ —anion type,⁸⁰ and for complex biological objects.^{81,82} There are grounds to believe that the cooperative mechanism of transport can also be involved in the case of some alkali metal cations.⁸³ All the systems listed above are characterized by relatively low degree of binding and low lattice energy. Apparently, this is important for the effective course of cooperative processes.

Proton conductivity

The proton conductivity (σ) in inorganic compounds is a striking consequence of the translational mobility of proton-containing groups. The ion mobility in solids is often studied by conductometry because experimental data obtained by this method are relatively easy to interpret and are highly significant from the practical standpoint. The conductivity can be found as the product of the translational mobility of hydrogen ions by the concentration of the corresponding defects. In individual compounds, proton defects are always formed in pairs (a vacancy and an interstice). As a first approximation, it can be considered that the energy of formation of this pair is close to the enthalpy of proton transport from H-bond acceptor to H-bond donor (ΔH). Therefore, the activation energy of conductivity increases with respect to the corresponding value for ion mobility by half the energy of formation of a pair of charged defects ($-\Delta H/2$). Thus, the difference between the proton-accepting abilities of the O atoms involved in the transport process is more significant. Typically, the plots for the calculated $\log \sigma$ values vs. the length of H-bonds for different ΔH values (see Fig. 5, $g-i$) have a clear-cut conductivity maximum at $R_1 \approx R_2$. The presence of additional possible H-bond acceptors surrounded by O atoms of the $\text{H}(\text{H}_2\text{O})_n^+$ ions results in a higher conductivity due to a decrease in the activation energy for the rotation of proton-containing groups. The highest calculated value of conductivity at 298 K, equal to 0.05 S cm^{-1} , can be realized for $\Delta H = 0$ and for H-bond lengths of $\sim 2.78 \text{ \AA}$. This is close to the maximum conductivity observed experimentally for $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ (0.16 S cm^{-1}).⁸⁴ The continuous three-dimensional chain of H-bonds between the O atoms of oxonium ions and H_2O molecules with an equivalent proton-accepting ability and a bond length of $\sim 2.8 \text{ \AA}$ creates the most favorable conditions for the proton transport. According to NMR data, the proton hydrate sublattice of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ exists at room temperature in a highly mobile (quasi-liquid) state. The rotational mobility is stimulated by the exceptionally low proton-accepting ability of the anion, and the high vibrational mobility increases the frequency of proton hopping. Apparently, this is why the experimental value of conductivity exceeds the calculated limiting value by a factor of ~ 3 . A favorable combination of the above-mentioned factors is found in high-water hydrates of hydrohalic, heteropoly-, and some other acids with $\text{p}K \ll 0$. These compounds tend to form clathrate structures including proton hydrates and anions. The high proton conductivity of these systems was found in a number of works.^{85,86}

When the absolute magnitude of ΔH deviates from zero, the proton conductivity rapidly decreases. This accounts for the fact that proton transport in most of low-

Table 3. Calculated and experimental values for proton conductivity of some inorganic compounds

Compound	ΔH /kJ mol ⁻¹	R_{O-O} /Å	$\sigma/S\text{ cm}^{-1}$		Ref.
			Calculation	Experiment	
H ₃ PW ₁₂ O ₄₀ ·29H ₂ O	0	2.8 (average)	0.05	0.16	84
H ₅ O ₂ Ta(PO ₄) ₂	0	2.73	1·10 ⁻³	1·10 ⁻³	61
H ₃ OIn(SO ₄) ₂	0	2.87	1·10 ⁻⁴	1·10 ⁻⁴	88
Zr(HPO ₄) ₂ ·H ₂ O	15	2.78, 2.8, 3.06	3·10 ⁻⁷	1·10 ⁻⁷	89
In(HSeO ₃) ₃ ·3H ₂ O	35	2.61, 2.77, 2.81	3·10 ⁻⁹	<1·10 ⁻⁸	90

temperature proton conductors takes place between equivalent O atoms.

Some examples demonstrating the legitimacy of the above calculations are presented in Table 3. Hydrates of heteropolyacids containing a large number of water molecules (H₃PW₁₂O₄₀·29H₂O and H₃PMo₁₂O₄₀·29H₂O) are known as the best proton conductors at room temperature. These substances are formed by freely packed spherical anions PX₁₂O₄₀³⁻⁸⁷ with a highly mobile "solution" of the composition 3H⁺·29H₂O situated between them. The average length of hydrogen bonds in this "solution" is 2.8 Å, and they are highly flexible, which creates favorable conditions for proton transport. The proton mobility in the crystalline tantalum hydrogen phosphate is limited by the rotation of proton-containing groups forming relatively short H-bonds with $R_{O-O} = 2.73$ Å.⁶¹ The monohydrate of indium hydrogen sulfate ($R_{O-O} = 2.87$ Å) has a close value of conductivity,⁸⁸ limited by the frequency of proton hopping along the line of H-bonds. The data on proton conductivity of crystalline zirconium hydrogen phosphate⁸⁹ for which $\Delta H \approx 15$ kJ mol⁻¹ are in relatively good agreement with calculations. In indium hydrogen selenite, the length of H-bonds is rather favorable for fast proton transport; however, the proton-accepting ability of its anion markedly exceeds that for H₂O molecules. This results in low proton mobility and high activation energy for the formation of proton defects, which accounts for the low conductivity of this compound. According to ¹H NMR data, translational mobility of protons starts to show itself in this compound only at room temperature.⁹⁰

The effect of the nature of the anionic sublattice

From practical standpoint, it is most important to identify the types of chemical compounds in which fast proton transport is possible. The data presented here imply that conditions optimal for high proton conductivity are found in solids with equivalent proton-accepting abilities of the electronegative atoms involved in the transport. In addition, the length of H-bonds in them should be close to 2.8 Å. This distance is typical of the H-bonds between H₂O molecules. Since the length of

H-bonds is determined, first of all, by the general pattern of the structure and by the proton-accepting ability of electronegative atoms involved in its formation, one could expect that the optimal conditions for proton transport would exist in the hydrates of acid salts and acids in which the proton-accepting ability of the anion is close to that of the O atom of the H₂O molecule ($pK \sim 1.74$). An alternative way is to choose systems with low proton-accepting ability of the anion and a high degree of hydration.

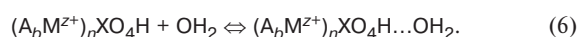
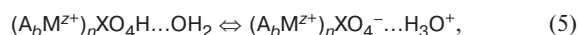
In addition, the solid electrolytes used for practical purposes should, undoubtedly, be relatively stable during operation. However, the clathrate hydrates with high contents of water readily decompose and the hydrates of strong inorganic acids have low melting points and their composition easily changes upon the change in the moisture content due to the low lattice energy. Acid salts can be much more stable. These salts are formed only in the case of polyhydric acids; however, strong inorganic acids are usually monohydric. Relatively stable are hydrogen sulfates, phosphates, and arsenates, *i.e.*, salts of acids that can hardly be regarded as strong. It is known that the proton-accepting ability of anions can markedly decrease upon coordination to various Lewis acids.^{91,92} These can be represented by either multicharged cations^{93,94} or the central atoms of anions with uncompleted coordination.^{95,96} When these complexes are formed, multicharged cations polarize the anions by pulling the electron density from the O atoms; as a result, the newly formed acid becomes much weaker. This is manifested most typically as a change in the tendency of H₂O molecules in the M(OH₂)_{*n*}^{*z*+} complexes to undergo acid dissociation, which depends directly on the polarizing ability of the M^{*z*+} cation coordinating them.⁹⁷

No quantitative data on the effect of the nature of the cations on the acidic properties of the anions coordinated to them in solids can be found in the literature (see, for example, Refs. 97, 98). We have estimated this effect using the results of ¹H and ³¹P NMR investigations of the proton distribution between an anion and hydrated species. The known pK values for anions coordinated by different numbers of cations (*n*) with different charges (*z*+) and the change of the anion proton-

Table 4. ΔH values calculated from NMR data

Compound	<i>n</i>	<i>z</i> ⁺	p <i>K</i>	$\Delta(\Delta H)$ /kJ mol ⁻¹
HIn(SO ₄) ₂ ·4H ₂ O	2	3	-1.3	18
H ₃ OTl(SO ₄) ₂	3	3	-2.3	24
Sn(HPO ₄) ₂ ·H ₂ O	3	4	3.3	52
H ₅ O ₂ Ta(PO ₄) ₂	3	5	-2.1	82

accepting ability with respect to that of the noncoordinated anion in aqueous solutions ($\Delta(\Delta H)$) (Table 4) show that the charge of the cations bound to the anion is the most important factor affecting the proton-accepting ability of the anion. Experimental data of this type can be obtained for a limited number of hydrates. Therefore, we calculated the changes in the proton-accepting abilities of tetrahedral anions in $(M^{z+})_nXO_4$ type complexes ($z = 1-6$, X = P, S, Cl) using the ZINDO1 method.⁹⁹ To attain a zero charge of the species considered and a completed coordination polyhedron of the M^{z+} cation, neutral or negatively charged species (A), namely, fluoride ions or H₂O molecules, were included additionally into its surrounding. The following reactions were considered:

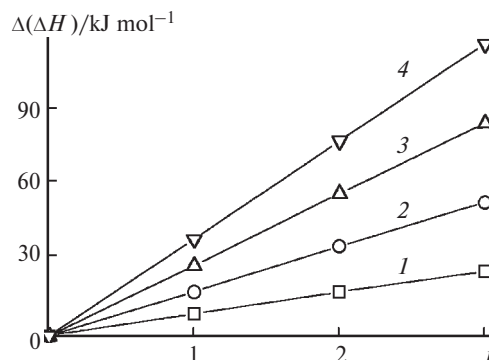


The calculated enthalpies of acid dissociation of the $(A_bM^{z+})_nXO_4H$ complex (reaction (5)) and of formation of the $XH \dots OH_2$ H-bonds (reaction (6)) and the changes in the enthalpy of reaction (5) compared to that of the corresponding sodium salt Na_yHXO_4 ($y = 0, 1, 2$) are presented in Table 5. All the absolute magnitudes of ΔH

Table 5. Calculated enthalpies of reactions (5) (I) and (6) (II)

M (<i>z</i>)	<i>n</i>	X	ΔH /kJ mol ⁻¹		
			I	$\Delta(\Delta H)^*$	II
Ti (4+)	3	Cl	197	655	-58
Ti (4+)	3	S	381	465	-59
Ti (4+)	3	P	640	210	-44
Zr (4+)	3	P	655	195	-46
Nb (5+)	2	P	711	140	-43
Nb (5+)	3	P	591	260	-52
Mo (6+)	1	P	745	110	-35
Mo (6+)	2	P	654	200	-50
Mo (6+)	3	P	555	295	-53
Na (1+)	2	P	851	0	-24

* Change in the enthalpy of reaction (5) with respect to that of the corresponding sodium salt Na_yHXO_4 ($y = 0, 1, 2$).

**Fig. 6.** Change in the proton-accepting ability of the XO_4^{y-} ions vs. the number (*n*) of the conjugated cations (M^{z+}) for $z = 3$ (1), 4 (2), 5 (3), and 6 (4).

determined in this way are, undoubtedly, overestimated, but the general trend in the variation of the dissociation energy appears quite reasonable and agrees with experimental data (see Table 3). The cation charge plays a key role in the decrease in the proton-accepting ability of the cation. In addition, this ability decreases almost linearly with an increase in the number of coordinating cations (*n*), which is consistent, for example, with the additivity of chemical shifts in the ³¹P NMR spectra for the coordination of PO_4^{3-} anions by different numbers of Al^{3+} and Zr^{4+} ions.^{100,101} Recall that the chemical shifts are determined by the electron density on the atom, which, in turn, is a function of ion polarization. Based on this reasoning and the experimental data listed in Table 4, we estimated the change in the proton-accepting ability in terms of enthalpy units ($\Delta(\Delta H)$) for tetrahedral XO_4^{y-} anions coordinated by different numbers of cations with different charges (Fig. 6).

The data presented here allow one to evaluate qualitatively the rotational mobility of proton-containing groups, the frequency of proton transport, and the proton conductivity level in various inorganic hydrates. The most rapid proton transport in acid salt hydrates containing tetrahedral cations is to be expected in hydrogen phosphates and arsenates in which the anions are linked to three five-charged cations (M^{5+}) or to two six-charged cations (M^{6+}); in chromates whose anions are coordinated to three M^{4+} ions; and in sulfates and selenates with anions coordinated to two or three M^{3+} ions. An alternative can be represented by compounds in which all the O atoms are coordinated to two multi-charged cations, for example, substances with the NASIKON type structure $(HZr_2(PO_4)_3 \cdot nH_2O)$.¹⁰²

It is quite natural that high proton mobility could also be discovered in some other acids or salts containing hydrated protons. In this review, we considered only general principles and mechanisms of proton transport, which could be helpful to experimenter chemists working in this interesting field.

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