Proton Conduction and Injection in Solids

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Contents

I. Introduction

The study of the electrical properties of solids is of considerable significance from two major points of view: firstly, for its own sake, since conducting, insulating, and semiconducting materials are of fundamental consequence for the major functions of energy storage and transmission and of communication; and, secondly, for the information such study can provide on the dynamic processes proceeding within the solid and at its surfaces and to develop understanding of those processes and their control for specific purposes. This interest in energy transmission and communication applies not only to industry and everyday life, but also to biological processes.

The electrical charge-carriers in solids are generally divided into two classes: ions and electrons. Ions are relatively massive, and ion transport is often described by a "hopping" mechanism of the ion from site to site. On the other hand, electron motion in metals and broad-band semiconductors is described quantum mechanically (though a "hopping" process is invoked for electrons in narrow-band semiconductors where they have large effective masses). The proton, small but massive compared with the electron, lies between these extremes and, consequently, there is special interest in examining its behavior as a charge-carrier in solids with the possible requirement of quantum descriptions in some situations, and particle descriptions in others. This interest is considerably heightened by the fact that the proton is the only ion which may be expected to form and be mobile in molecular organic solids, and hence may play an important role in intramolecular biological processes.

This paper reviews the evidence for proton conduction and injection in solids, inorganic, organic, polymeric, and biomolecular, including ice, the solid of major interest in the field of proton conduction. Consideration is given to the role of proton conduction in some physical and biological processes. The mechanisms proposed for conduction in the various solids, particularly cooperative proton transfer, are discussed, and an attempt is made to correlate this information to produce a set of necessary criteria for proton conduction.

Only two brief general reviews of proton conduction or injection have been published[1,2] and, although there is a large literature describing proton conduction, the subject receives scant mention in texts on electrical properties[3-10] or on hydrogen bonding,[11-13] except in respect to ice. There are, however, some brief reviews on biological aspects which will be mentioned at the appropriate place in this paper. It is hoped that one result of this review will be that the common features of proton conduction in solids, here high-lighted, will provide a basis for further understanding of proton transfer processes in all their ramifications.

A. Scope of the Review

In conformity with the title of this review, the treatment and the literature survey deal with electrical conduction

properties in crystalline solids. Other properties of the materials considered, such as nuclear magnetic resonance (nmr), infrared absorption (ir), and dielectric behavior, are referred to insofar as they illuminate the mechanism of the conduction; this implies that the treatment of such properties is selective and is·not intended to be comprehensive. This is especially to be noted in respect of the vast literature on ferroelectrics, where correlation of information from all techniques for all the relevant materials requires a large book.[19] Furthermore, the special problems of surface layers (which generally implies those of adsorbed water in this situation), of glasses, of polymers, and of biological systems will not be accorded full treatment, but will be examined only insofar as they display properties of particular interest.

In view of the absence of a comprehensive prior review of proton conduction, the literature referring to crystalline solids is fully discussed (to about Sept/Oct, 1973), except in the case of ice on which the literature is so voluminous that comprehensive coverage would be inappropriate for a general review. However, the more recent literature on ice is reviewed, and references which give access to the earlier literature are included. The literature references are arranged to keep those pertaining to a particular material or group of materials in numerical sequence.

B. Role of Proton Conduction

As mentioned in the Introduction, proton conduction may play a part in a number of processes which will be detailed as they appear in the review below. It is worthwhile, however, to collect a few such examples together so that they may be noted in explanation of the interest in the phenomenon.

The clearest direct application of solid-state proton conduction occurs in situations where there is a requirement to transmit hydrogen across some intervening barrier. This occurs in fuel-cell technology with $H_2|O_2$ cells where materials with good proton-conducting ability, but blocking to electrons and insoluble in water, would be of great value.[1] Correspondingly, a number of specific biological processes appear to depend on proton transfers:[14-16] for example, photosynthesis, where a primary process involves proton liberation and migration across a membrane; certain enzymatic processes; transport across phospholipid membranes; and perhaps in the mechanism of vision, associated with rhodopsin. The catalytic aspect appears also in inorganic applications, where proton transport may be required on or through the solid catalyst in hydrogenation and dehydrogenation processes, while many thermal decompositions[17,18] involve the loss of water, perhaps following an initial movement of protons, so that examination of proton conductivity can aid in elucidation of the process.

Ferroelectrics[19-21] and electrets depend for their properties on a polarization of the medium; if this medium can permit proton conductivity (as it apparently does for a number of hydrogen-bonded ferroelectrics, at least in their paraelectric phases), then the value of the medium for dielectric applications will be reduced. Thus, knowledge of conditions which permit proton conductivity could be of service in this technology.

II. Identification of Proton Conduction

A. Electrodes

Electrical equipment operates, of necessity, by the passage of electrons through metallic conductors; metal electrodes must then be in contact with the proton conductor for a continuous current to be able to pass. This immediately brings to the fore one of the basic problems with any ion conduction process, for electron–ion exchange must occur at the interface in order that a current flow be maintained.[3,22-25] This exchange process may occur with varying degrees of ease, from complete "blocking," when no exchange at all occurs and all the potential drop between the electrodes is eventually concentrated as a "space charge" at the metal–ion conductor interface, to the opposite extreme of a completely "ohmic" contact, which exhibits no potential drop at all, in whichever direction current is flowing. "Blocking" action must break down if sufficient potential is applied, while the truly "ohmic" electrode is an ideal to be aimed for since the concept implies that no energy whatsoever is required for the electron–ion exchange; real metal electrodes applied to ion conductors thus will exhibit varying degrees of blocking. This will affect the measurement of conductivity of any ionic solid, but may not be significant for a high resistance solid with ready ion injection and discharge, for, in such a case, most of the potential drop is across the solid.

The problem of the effects of discharge at the electrode contact may be partially avoided by undertaking transient measurements,[363i,499] where the current flow following the switching-on of a voltage is followed. With blocking electrodes, all the effects observed must arise from intrinsic charge motion combined with dipole reorientation. It is noticeable, however, that even in these circumstances interpretation may not be simple, and may require correlation with many other experiments. The other extreme approach to the problem is to apply such large fields to the sample that all free charge-carriers are swept out, and the remaining saturation current corresponds, in the absence of charge injection, to the formation of new charge carriers by dissociation.[387] This high-field experiment, while temptingly simple of interpretation, carries the danger of the high applied fields inducing processes which are normally absent—a Wien effect.

The more usual approach has perhaps been simply to ignore the electrode problem and rather hope to identify the ion conduction process, when later work can establish the parameters of the conductivity. However, a large number of workers have made positive efforts to minimize electrode effects by devising appropriate electrode systems. Although the description which follows is couched in general terms, it must be appreciated that most of the effort with proton conductors in this direction has been made in respect to ice, and the systems have often been tested for ice only; whether or not they work for other materials must be determined in each case—indeed, it is not even clear that they work as intended for ice![16]

The general techniques developed parallel rather closely the techniques applied in the study of semiconductors, adapted to the circumstances of the proton conduction. The simplest approach to avoiding electrode polarization effects is to use large current electrodes together with a pair of fine potential probes placed in the current path. With minimal current drawn through these potential probes, the current lines are expected to be little disturbed; this was the method used by Johnstone (1912),[379] the first investigator to make quantitative measurements of the electrical conductivity of ice, and by others more recently.[362e,387,388] However, this approach cannot be entirely satisfactory because the barriers to discharge occur equally at the potential probes, and polarization will occur when current is drawn. This may be

reduced (as at all electrodes) by the presence of a "pool" of defects in the solid near the electrode (formed during the freezing-in of the electrode in the case of ice), but then the difficulty still remains as to what exactly the potentials being measured refer.[384]

Thus, a more direct attack on the problem is frequently undertaken. This takes the form of using electrodes which can act as sources or sinks of protons. Palladium metal, by virtue of its ability to absorb and transmit hydrogen as well as to conduct electronically, provides the most convenient of such "protodes"[354,386] and has been used by a number of workers; to provide a proton source, the palladium is first induced to absorb hydrogen, usually by being made the cathode in an electrolysis cell with a weak hydrochloric acid solution as electrolyte.[362e,386d] The palladium is often coated on the surface contacting the sample with a deposit of palladium black, in order to catalyze the proton exchange while, in one case,[362f] an additional thin (ca. 200 Å) layer of palladium was evaporated onto the sample surface to improve the contact. Injection may be followed by using labeled carriers, such as deuterons.[16b,386d] While such palladium electrodes appear to work well with ice, there is evidence to suggest that they may not be suitable for proton exchange at all materials,[283] so that their use cannot be regarded as the definitive solution. Furthermore, it is always possible that such an electrode injects electron holes rather than protons,[16] and it is desirable to demonstrate the physical presence of injected hydrogen, by using deuterium or tritium.

Another procedure for forming protodes has been to prepare a proton conducting layer of low resistance at the sample surface, so that electron–proton exchange can occur more readily in that region. This can be done in various ways, most of them suitable for ice but less suitable for other water-soluble, proton conductors. Thus, an HF-doped layer may be frozen onto the pure ice surface,[388c,d] or ion-exchange membranes may be pressed onto the surface.[386c] A procedure which avoids contamination was used by Eigen, et al.;[387] they froze a sample of water in a U-shaped container with a temperature gradient near its ends so that the ends were still liquid and could provide a transition between the platinum electrodes and the ice. This technique, however, introduces the problem of a temperature gradient and can only be used near the freezing point of the material. Aqueous electrode layers could similarly be used to form protodes at proton conductors other than ice, in the form of a saturated solution of the sample.[233] This introduces problems, however, as there is a danger that solvent will seep through cracks or channels in the sample and, on changing temperature, it would be difficult to ensure saturation and steady conditions. An alternative procedure has been reported in a variation of Tubandt's method for ion transport number determination[25] in solids: a known proton conductor (imidazole[283] or $NH_4H_2PO_4$[164]) has been used as a protode for the sample to be tested, with metal electrodes to complete the "sandwich," in the following sequence: anode (metal)–proton source–sample–proton sink–cathode (metal). The proton sink can be omitted when the hydrogen generated there is to be collected, rather than absorbed. This system, with suitable materials, avoids chemical reactions at the sample interfaces and the problems associated with the presence of liquid electrodes, but has rather a high resistance and must await the discovery of a really low-resistance proton conductor, to act as protode, for its full potential to be developed. A possible candidate[26,27] for such a role is $LaNi_5$ which is a good metallic conductor and takes up large amounts of hydrogen rapidly at 25°. These techniques for ion conductors, in general, have been extensively discussed.[22-25]

B. Surface Conduction

The surface of a solid is peculiarly susceptible to effects uncharacteristic of the interior: in covalent crystals there may be "dangling" bonds;[28] certain faces of crystals display molecular groups of one type only and so are far from representative of the bulk;[29a] and, especially in respect of ice, there may be a disturbed surface layer.[363a] A crystal with charged defects will, in thermal equilibrium, have a space charge adjacent to its surface which will produce an electric field, even in the absence of an applied voltage.[30] For these reasons the possibility of a surface conduction behavior which is very different from that of the bulk must be carefully considered at all times. In particular, measurements on powders and polycrystalline samples, with their large surface areas, are generally regarded with some suspicion. The method used to eliminate surface conduction in electrical measurements is the application of an earthed guard ring to the low voltage electrode;[31-33,500] this guard ring surrounds the measuring electrode entirely, without coming into contact with it. Surface currents from the high electrode flow into the guard electrode and are allowed to bypass the measuring circuit, which detects only the current passing directly between high and low electrodes. The guard and low electrodes are held as closely as possible to the same potential so that no current flow will occur between them. An additional benefit conferred by the guard ring is the elimination of edge, or fringe, effects. Provided that the gap between low and guard electrodes is small, this gap will not disturb the current flow lines, which will be distorted only near the outer fringes of the sample; but this fringe current is led to the guard electrode and is not measured. (Surface conduction and fringing effects are phenomenologically identical, so that the distinction may really be redundant.)

Although the guard ring should, in principle, always be used, it can sometimes be shown by suitable experiments to be unnecessary. With powders and materials having conductive internal surfaces, its use may give illusory confidence since the internal surfaces may carry current directly to the low electrode, short-circuiting the path to the guard electrode.[488]

C. Phenomenology of Conduction

Once the true, bulk electrical current has been established, its proportionality with the applied voltage may be tested and the applicability of Ohm's law thus confirmed (but see section II.D. below); if this can indeed be confirmed, it becomes meaningful to talk of a conductivity, σ. This conductivity is occasioned by the motion of charge-carriers of charge q_i, concentration n_i, and mobility μ_i, so that, with independent migration of the charge-carriers

$$\sigma = \sum_i \sigma_i = \sum_i n_i q_i \mu_i$$

The principal method by which the conductivity phenomena are unravelled is variation of the independent contributions to the conductivity either by "doping" the material with conductors of various kinds or by exciting intrinsic charge-carriers (and, to a lesser extent, by varying their mobility) through temperature alterations. The

excitation of ionic charge-carriers is generally an activation process, so that the conductivity will vary approximately exponentially with the absolute temperature, i.e.

$$\sigma T = \sigma_0' e^{-E'/RT}$$

where R is the universal gas constant, while σ_0' and E' (the activation energy) are constants found as best-fit parameters to the experimental data. The above equation is often simplified to

$$\sigma = \sigma_0 e^{-E/RT}$$

when it is felt that the quality of the results do not justify the sensitivity to temperature effects implied by the former equation. This simplified equation yields values of the activation energy which are too large by an amount RT, that is, by about 5% of the typical activation energy of 10–15 kcal mol^{-1}. Room-temperature conductivities which are typically encountered range from values as low as 10^{-15} ohm^{-1} cm^{-1}, for benzoic acid, to a high of 3 × 10^{-4} ohm^{-1} cm^{-1}, observed for oxonium perchlorate using alternating current.

D. Electron, Ion, or Proton Conduction?

A major problem in the field of proton conduction is definitive proof that charge transfer in the solid[10] occurs by motion of protons. A number of criteria are generally applied which, taken together, may prove to be more or less convincing but which can nevertheless be ambiguous. These are discussed below and are (1) observation of a slowly decaying current (polarization) or low-frequency dielectric absorption (a Maxwell–Wagner process); (2) hydrogen gas evolution in coulometric measurements; (3) charge injection and extraction; (4) a variety of other methods, including determinations of thermoelectric power, diffusion potentials, cell potentials, and the Hall effect.

1. Time-Dependent Polarization (Including Maxwell–Wagner Dispersion)

No chemical reactions occur at the electrode surfaces of electron conductors which are carrying current; electrons or holes may be injected or extracted[46,53] but, under steady conditions, switching transients will gradually die away and a time-independent steady-state will subsist. The characteristic times of the transients will typically be short ($t = (RC)^{-1}$, where R is resistance and C is capacitance, for a noninjecting system) and perhaps of the order of seconds or less for an injecting system,[34] though the time to thermal equilibrium could be exceedingly long.[53]

For ionic conductors, one of the characteristics (as mentioned in section II.A) is the existence of chemical reactions with other than completely blocking electrodes,[35] and space charge polarization with even partially non-ohmic electrodes. Chemical reactions will, of course, continuously alter the characteristics of the sample–electrode interface if reaction products are allowed to accumulate, or will eventually reach a more-or-less steady state, if all the reaction products are gaseous and depletion of the sample by the reaction is not serious. In any event, as the result of deterioration of the contact, chemical reaction is likely to produce a relatively slow increase in total sample resistance with time; in certain special instances, there may be a decrease in resistance with time, as in experiments on the electrical transport

properties of AgI where silver is deposited,[3,4,25] but these circumstances do not apply in proton conductors.

The second cause of a falling current in a system undergoing ion conduction with partially blocking (i.e., non-ohmic) electrodes, is the space charge polarization previously mentioned, arising from the accumulation of charge-carriers at the sample–electrode interface; this accumulation occurs because the rate of discharge of charge-carriers does not equal their rate of arrival at the electrode, or because the rate of discharge of positive and negative carriers is not equal, or because the rate of injection of charge-carriers does not equal their rate of transfer or of discharge;[36] the accumulated charge is termed a space charge by analogy with the charge which develops within a vacuum tube, in front of a heated cathode. The build-up of space charge will continue while current flow proceeds until there is sufficient potential drop across the space charge region to force charge-carrier discharge, and eventuate in a steady-state condition where a steady, but reduced, current flows.

The sequence of events following application of a voltage across an ion conductor may be described as follows.[377d]

"(a) The applied field is distributed uniformly across the dielectric as predicted by a homogeneous volume polarization and unhindered current transfer.

(b) The applied field becomes distorted by the development of an anode and/or cathode fall (space-charge polarization develops).

(c) The total carrier content of the dielectric begins to deviate from electroneutrality by discharge and/or injection of carriers at one or both electrodes."

For these reasons, then, one of the characteristics of ion conduction is often taken to be the observation of a decay in current over an extended period (Eley and Leslie[422a] choose 1 hr or more). As is implicit in the present discussion, however, the extent of polarization may be very dependent on the system under investigation and the details of electrode contact, so that the apparent absence of polarization, while indicating the need for caution in interpretation, need not exclude ion conduction. The presence of time-dependent polarization creates serious problems in respect to conductivity measurements, for it is difficult to determine what value of the current is characteristic of the conduction process. An initial rapid polarization may indicate that the initial currents are contributed to by dielectric displacement currents,[37,38] so that the final stable currents (if such occur) should be observed. On the other hand, as noted above, development of space-charge polarization distorts the internal fields so that initial, transient currents should be determined before distortions of the field can develop.[363i,j,377] It is probable that, with different materials and different temperatures, one or other of the effects may be the more important[39] so that a detailed investigation of each situation may be required.

The above discussion on polarization, while couched in terms appropriate to dc conduction, applies equally to measurements with alternating currents.[40,41] At low enough frequencies (which may be as high as 100 Hz or more), charge carriers will have sufficient time to accumulate at alternate electrodes during each half-cycle so that the sample with blocking electrodes behaves, in effect, as a single large dipole whose orientation is reversed during each half-cycle. Such an effect is known in the language of dielectrics as a Maxwell–Wagner polarization, and has the same frequency dependence as the standard Debye–Pellat absorption which arises from the relaxation of molecular dipoles under the influence of an

alternating applied field.[42] As a result, low-frequency dielectric absorption results in some ambiguity of interpretation, and additional experiments (perhaps with a variety of electrodes, and different sample thicknesses, or with doped samples) may be required to identify the origin of the absorption. More complex effects, associated with discharge at the electrodes, have been discussed in considerable detail and must also be taken into account as required.[43-47]

2. Coulometric Measurements

Perhaps the most direct method for determination of the nature of the charge-carrier in protonic conduction has been the quantitative determination of the electrochemical products of conduction when current is passed between the electrodes and the gas evolved is collected, generally over mercury.[301] The identity of the gas is determined, and confirmed as hydrogen, by deposition of Pd from $PdCl_2$ solution[239] (there is a danger here of mercury contamination which can also cause Pd deposition), by combustion,[436] by diffusion through a Pd septum,[434] or by mass spectrometry.[283] Finally, the volume of gas collected is compared with that expected from Faraday's law of electrochemical equivalence, the difference being attributed to gas losses (for instance, solution in the mercury)[48] and to a contribution by other charge-carriers to the conduction process.

A serious ambiguity may occur. The identification of a product of chemical reaction (the hydrogen) is taken to be direct proof of an ionic contribution to the conduction, in proportion to the transport number of the ion involved. The discharge of an ion is, however, not necessarily as significant as has been taken to be the case in the past, for the ion which is discharged may not be the charge-carrier.[1,188] This situation is well known in electrolyte solutions; hydrogen gas is evolved at the cathode of a sodium salt solution, even though it is the sodium ion which transports the charge. Thus the electrochemical formation of hydrogen gas is really only an indication of ionic conduction; identification of conduction by protons specifically will require further evidence.[24,145] Even in ice, where no other ion than H^+ can reasonably be regarded as mobile, the evolution of hydrogen gas could conceivably arise from the conversion at the electrode of lattice defects into ionic defects, which are then discharged.[377]

3. Space-Charge Polarization: Voltage Effects[29b,49-54]

An insulator will generally contain a certain concentration of volume-generated current carriers and the flow rate of these carriers will increase in proportion to the applied voltage, to yield an ohmic behavior, from which the bulk conductivity may be assessed. Depending on the work functions of the insulator and electrode, the electrode may be able to inject charge-carriers into the insulator[49] (when it is described as "ohmic" in the language of space-charge theory, or as a "protode" in the present description). If injection should occur, a space charge of injected charge will be developed in the insulator, in front of the injecting electrode, and the application of a voltage will yield space-charge limited currents (SCLC) from this injected charge, if one regards the injected charge as roughly independent of the volume-generated charge.[49] The space-charge limited currents increase as the square (or higher power) of the applied voltage, so that at sufficiently high voltages the currents will increase from ohmic behavior to "square-law," or Child's law, de-

pendence. This transition occurs when the injected and volume-generated charge concentrations are of similar magnitudes. At still higher voltages, sufficient charge may be injected to fill all charge-carrier traps, at a voltage termed the trap-filled limit, when the current will rise reversibly as a very high power of the applied voltage. Space-charge theory for the simple case of a trap-free insulator with injected charge of a single type with mobility, μ, yields the result

$$j = (9/8)\,\varepsilon\mu V^2/d^3$$

where j is the current density, ε the permittivity, V the applied voltage, and d the sample thickness. The dependence of j on (V^2/d^3) is to be noted. Ohm's law, written in a corresponding form is

$$j = n_0 q V/d$$

where n_0 is the concentration of volume-generated charge and q is the charge carried by the current-carriers. Charge-carrier concentrations, n_0, and trap concentrations, n_t, are obtained from the transition voltage, V_t, between the Ohm's law and the square law regions, and from the voltage of the trap-filled limit, V_{TFL}, from the simplified theory, as follows

$$n_0 = 2\,\varepsilon V_t/(qd^2)$$
$$n_t = 2\,\varepsilon V_{TFL}/(qd^2)$$

The former equation should, in fact (even on the simplified model), be replaced[55,56] by a more complex expression.

These results are utilized, in proton conduction practice,[305] by examining the current–voltage plots for the first deviations from linear behavior, from which a very qualitative evaluation of the volume-generated carrier density may be obtained (this value is, of course, very much dependent on sample perfection and conditions). From the square-law region, if found, a value for the injected carrier mobility may be calculated, while from the value of V_{TFL} the trap concentration may be determined. This analysis presupposes that stable currents are being evaluated. Transient currents, from injected charge carriers, may also yield mobilities.[53,363n]

While space-charge theory has often been invoked in evaluation of the conductivity parameters in proton conductors, there is only one instance, in ice, where a full space-charge current–voltage curve has been obtained.[385a] In the situations where this has not been obtained, the results can only be regarded as a qualitative indication of the space-charge behavior, and it is difficult to know what reliance can be placed on the mobilities so evaluated.

4. Other Methods

a. Thermal Gradients

If a thermal gradient is applied to a conductor, an electric potential will be generated following on the increased thermal motion of the heated charge-carriers. Using the methods of irreversible thermodynamics, some information on the relative concentrations of the different kinds of charge-carriers may be obtained from the sign and value of the thermoelectric potential.[57,359a] Further information may be obtained by doping the conductor with impurities to generate various kinds of defects selectively, by which means the effects of each kind of defect may (hopefully) be isolated.[358,359a]

b. Concentration Gradients

Charge flow may be induced by other means as well. An impurity gradient, created by doping, or by conjunction of conductors with different impurity contents, will induce a charge flow, in suitable cases, and set up an electrochemical potential which can be measured quite readily.[58] There is, as well, a mass flow associated with both the above situations,[383] but the amount of the mass change will generally not be measurable in the materials under consideration although it is measurable with alloys, as the Kirkendall effect; potential differences are much more readily measured. This method of concentration gradient-induced charge flow has been used to determine the characteristics of ice, and to check the results against the theoretically expected values.[359a]

Yet another method of establishing measurable electric potentials is possible, in a procedure which is common in the study of transport numbers. This procedure is to establish different charge-carrier concentrations at opposite faces of a sample of the conductor (perhaps by applying different pressures of a gas—hydrogen for proton conductors—or by applying different proton conductors at the opposite faces, each supplying a fixed electrochemical potential of the proton). The ratio of the measured emf to the thermodynamic emf, calculated assuming proton conduction alone, will give the ionic transport number directly, provided that equilibrium is attained at each electrode and that no other open circuit means of hydrogen transfer occurs.[22-24]

c. Hall Effect

A charge-carrier moving through a magnetic field is subject to forces which deflect it from its direct path; this is the Hall effect. Such a deflection is measured as a Hall voltage (or current) normal to the direction of charge carrier motion when this is itself normal to the lines of the magnetic field. The magnitude of the Hall voltage is determined by the number and mobility of the charge carriers, while the sign is determined by the sign of the charge-carriers. Unfortunately, a Hall effect measurement is difficult[59] in a poorly conducting material and the results may be ambiguous. Firstly, while electrons will give a negative Hall voltage and protons a positive voltage, positive voltages are also generated by electron "holes" in the conduction band, which behave as positive charge-carriers. Secondly, the Hall mobility may be different from that determined from conductivity experiments, in situations where the conduction occurs together with a trapping process. The conduction experiment determines the average (drift) mobility of the charge-carrier over trapped and mobile states together, since the observation is, in effect, of distance moved in unit time. The Hall voltage, however, is generated only when the charge-carrier moves, so that the Hall mobility must exceed the drift mobility; in the case of ice, a factor of 20 has been obtained,[385b] although the value of the results is now disputed because of the unexpected interference of the surface conductivity and polarization of the ice.[363j]

E. Indirect Dynamic Evidence for Proton Conduction[13]

A number of techniques besides dc conductivity, emf, and electrolysis procedures are available for studying hydrogen bonding, in general, and the freedom of protons to move within a crystal, in particular. Among these are diffraction measurements, which can show the distribution of a proton (or deuteron) over the sites available to it. However, such measurements do not distinguish between static and dynamic distributions while the displacements involved are small and require accurate analyses. Techniques which provide information more directly on dynamic processes are infrared (ir) and Raman spectra, nmr spectra and relaxations, epr, neutron inelastic scattering, dielectric spectra and relaxations, ultrasonic spectra and mechanical relaxation, and diffusion.

1. Ir and Raman Spectra

Ir and Raman spectra are rather readily obtained and can often be associated with particular vibrations within the crystal. Interpretation can, however, be a problem, and misleading results may be obtained. A particularly apt example of the difficulties is imidazole, in which there is in the ir spectrum a broad NH band with considerable fine structure. Zimmermann[60,273] has discussed this spectrum in terms of a rapid proton-tunnelling process across the $N—H \cdots N$ bond, but it has been found that models which involve coupling between the $N—H$ and other vibrations can yield equivalent results,[274] while the Nmr line shape is inconsistent with proton tunnelling.[276] Fripiat, et al.,[101a] who have used both ir and nmr techniques in their studies of proton motions in solids, have found ambiguities in interpretation of ir spectra and suggest that, in the complex systems which are considered (adsorbed species in their case), it is desirable to use infrared (and dielectric) spectroscopy to obtain a first approximate model for the system "and then, in the light of this information, to compare the expected nuclear magnetic relaxation times of the hydrogen nuclei ... to those obtained experimentally." This is not to say that ir and Raman spectroscopy are not relevant to studies of hydrogen bonding, for indeed they have been fundamental techniques in this regard. However, they relate to properties of the proton within the bond[13,394] and much less to its freedom to break loose from the bond, as is required for conduction to occur. As a result, there are few important ir studies which bear directly on proton conductivity.

2. Nuclear Magnetic Resonance

Nmr provides a potentially much more useful technique for studying proton and deuteron movements in solids, partly because the lifetimes of the species involved are expected to lie within the range best suited to study by this technique.[104] Therefore, water molecule and proton motions in hydrogen-bonded systems have been extensively studied by nmr techniques. This is particularly applicable to the study of ferroelectric transitions where the quadrupole splittings of nuclear magnetic lines provide a powerful method for the study of such transitions, while lifetime and relaxation data (in the laboratory frame and in the rotating frame) provide direct information on the dynamics of the processes. Thus deuteron spin–lattice relaxation time studies show the existence of two basic reorientation times in KD_2PO_4-type hydrogen-bonded ferroelectrics:[176,186] a very fast one (10^9–10^{12} Hz) connected with deuteron motion within the hydrogen bond, and a low-frequency one (10^3–10^5 Hz) connected with exchange of deuterons between different hydrogen bonds due either to spatial diffusion of deuterons or hindered rotations of the D_2PO_4 groups. The different sorts of information available from deuteron and proton magnetic resonance in solids have been summarized by Blinc.[61] Together with these advantages, however, there are a number of drawbacks to nmr methods which must be considered in their evaluation.[13,62] Insofar as the

spectra are concerned, use of a polycrystalline sample yields, in general, a structureless absorption spectrum from which a single quantity, the second moment, is usually derived. Since this relates to all spin–spin interactions in the crystal, interpretations may be difficult except in certain simple cases. When single crystals are used, there are difficulties with crystal orientation, low signal-to-noise ratio, overlap of resonance lines, and the effects of thermal motion. With respect to nmr relaxation times, interpretation of the results is necessary, and their relationship to conductivity cannot be unequivocally determined. In particular, conductivity may depend on defects present in too small a concentration to effect relaxation, and alternative mechanisms may be operative.

3. Electron Paramagnetic Resonance

Epr (and endor) measurements can only be made if a free radical is first created by irradiation. The data obtained can be interpreted to yield information on the possibility of proton transfer across a hydrogen bond.[61,63,277] The results relate to the structure of the radical, and studies of the spectrum as a function of time and temperature can yield information on proton exchange with neighbors. A principal difficulty is that the observations are of the radical only, and its equivalence to the normal molecule must be inferred.

4. Cold Neutron Scattering[13]

Inelastic scattering of slow ("cold") neutrons provides information on the energy levels of the hydrogen bond systems and on the rotations of hydrogen-containing species, by determination of the energy gain or loss after neutron scattering. This is facilitated because the incoherent scattering cross-section of hydrogen is particularly large. The technique is rather new, and results relevant to proton conduction are limited.

5. Dielectric Dispersion[29b,42,64-68]

Measurements with ac bear the closest relationship to dc conductivity and electrolysis measurements. Dielectric dispersions will indicate dipole reorientations and, through the change in the relaxation time as a function of temperature, will yield an activation energy for the dipole reorientation. Conductivity will appear as a dielectric loss which is inversely proportional to the measuring frequency; however, space-charge polarization at blocking electrodes may cause difficulties.[43-47] Debye relaxations can also be mimicked by two-phase systems in which one phase is conducting and the other not, in a true Maxwell–Wagner polarization.[42] To these complications must be added the comment that dielectric measurements are "blind" to nondipolar processes, so that a solely dielectric interpretation of a conducting phenomenon must be incomplete.

It is clear from the discussion on dielectric phenomena that a dielectric "conductivity" measured at a single frequency can supply little information on a process involving conduction[1] and that, if there should be a dielectric dispersion at that frequency, the results may be positively misleading. The error of making and attempting to interpret single frequency conductivity measurements will be noted in a number of the reports described below. Furthermore, dielectric measurements are generally made with two-electrode systems so that surface conductivity may be a serious interference.

The static (radiofrequency and lower) dielectric constants and related properties of a large number of inorganic solids have recently been compiled by Young and Frederikse.[457]

6. Ultrasonic and Mechanical Measurements

Ultrasonic measurements and mechanical relaxation measurements may be used to study defects in solids, and may be related to proton motion if this motion is related to that of such defects.[358,377d] These measurements are difficult to perform on crystalline materials and subject to much interference from crystal imperfection. They have, therefore, seldom been applied to the study of proton motion, except for the case of ice where the mechanical properties have an inherent importance.

7. Diffusion[58]

Study of the kinetics of self-diffusion by use of radioactive tracers can be a useful adjunct to conductivity measurements, in order to examine the mode of the conduction by comparison with the diffusion. Unfortunately, it has often been observed that the processes occur in quite different ways, the diffusion apparently being a whole-molecule interstitial process which involves no net charge transfer, as opposed to the charge transfer which occurs during conduction.

8. Assessment

Conduction in poorly conducting media may depend on the presence of defects in small concentrations (perhaps 1 part in 10^6), whereas techniques such as X-ray, electron and neutron scattering, ir, nmr resonance and relaxation, and dielectric dispersion are insensitive and are only able to detect species present in relatively large concentrations, say 5%. They are, therefore, unable to detect defects in normal concentrations and rely for their utility on the presence of large-scale effects.

It must thus be noted that the techniques useful for the study of dynamic proton processes in solids are necessarily incomplete insofar as conductivity is concerned, and must be regarded as supplementary to the fundamental conductivity measurements. To paraphrase, the proper study of conduction is conductivity. This is stated in full appreciation of the many misleading facets of conductivity measurements, most especially the lack of ohmic electrodes. It is only when electrodes can be regarded as ohmic without doubt (and no proton electrode can be so regarded) that the effects of other rate-determining processes in the conductivity, such as internal charge-generation or molecular rotation, can be studied without interference.

III. Cooperative Proton Transfer

A. Classification of Materials According to a Hydrogen-Bonding Scheme Involving Cooperative Proton Transfer

A principal function of the present report is to display the effect of hydrogen bonding on the electrical conductive properties of a large variety of materials, inorganic and organic, ionic and molecular, discrete and polymeric. It is thus convenient to use a hydrogen-bonding scheme to classify the materials into appropriate groups. Attempts have been made by a number of authors to develop a satisfactory scheme of this kind but, in the words of Hamilton and Ibers,[13] "this is an area where further systematic work would be useful"!

The classification of materials which is used here is as follows: (1) materials lacking stoichiometric hydrogen

(section IV.A.1); (2) materials without hydrogen bonds (section IV.A.2); (3) materials with isolated hydrogen bonds, or closed circuits of such bonds (section IV.B.1); (4) materials with chains of hydrogen bonds, broken by intramolecular links (section IV.B.2), e.g., in KH_2PO_4
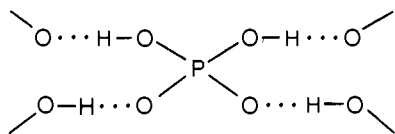
(5) materials with linked chains of hydrogen bonds (section IV.B.3), e.g., in alcohols
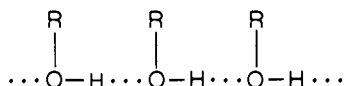
(6) polymeric systems (section IV.C); (7) biological systems, including biopolymers (section IV.D).

This scheme of classification is geometrical and has the defect of sometimes separating materials which are chemically similar, as noted in a similar context by Wells.[69] However, the solid-state properties are paramount in this discussion, and it is believed that the structural relationships[13,17,69-78] are what must determine the classification scheme. On the other hand, this scheme may not be suitable for other purposes and is not intended for general application.

B. Mechanism of Conduction by Cooperative Proton Transfers

The geometrical classification of hydrogen-bonded systems outlined above follows, in spirit, a scheme briefly proposed by Wirtz[79] in describing systems in which cooperative proton transfers might occur. The conception is that in a linked chain of hydrogen bonds
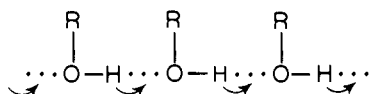

it is possible for a cooperative proton transfer to occur, as indicated by the arrows, to yield a hydrogen-bond chain in reversed orientation
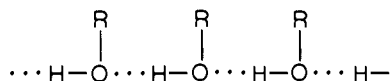
The net effect of this process is to transfer a hydrogen atom from one end of the chain to the other; if this transfer should follow on from the introduction (injection) of a proton at the left-hand end of the original chain, or from the removal of a proton at the right-hand end, then the charge of the proton will have been conveyed to the opposite end of the chain following the transfer. Such a process may be conceived of as happening very rapidly if the protons, as a result of their mutual interactions,[60] are able to tunnel across the hydrogen bond in a concerted fashion. Evidence for this cooperative transfer would be a large conductivity in the hydrogen-bond chain direction, compared to the conductivities in other directions, and an exceptional mobility of the proton in the conduction process. Such a fast proton transfer with tunnelling may be discussed equivalently by considering the protons to exist in a proton conduction band, so that the material is a "proton semiconductor."[362h] This conception is the basis

of the quantum mechanical treatments of proton conduction.[80-89,458]

However, the proton transfer process is an incomplete description of conduction, for the hydrogen bond chain is left at the end of the proton transfer in a reverse orientation from that in which it originally was, and is unable to permit any further proton transfer in this condition. Therefore, it is necessary to postulate a reorientation process for the chain, as follows
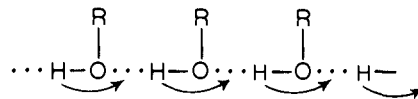
Whereas the original cooperative charge-transfer process could be regarded as the motion of a charged defect along the chain, the reorientation process can be regarded as the sequential motion of an orientational (or Bjerrum) defect along the chain:[359a,369] either the motion of a doubly occupied hydrogen bond known as a D defect (for "Doppelbesetzung") to the right, or the motion of an empty hydrogen bond known as an L defect (for "Leerstellen") to the left. Provided that the orientational defects are in large concentration (the majority carriers, as they are believed to be in pure ice) and able to move freely to effect reorientation, most hydrogen bond chains will remain in suitable orientation for transfers of ions (the minority carriers in ice). The rate-determining step in conduction under such conditions will be either the tunnelling rate of the protons in the transfer process or, especially under high field conditions, the rate of spontaneous formation or injection of ionic defects (excess or defect protons).

While this reorientation mechanism may be adequate for systems containing directly linked hydrogen bonds (type 5 of the classification), another possibility must be considered, especially in regard to systems containing chains of hydrogen bonds broken by intramolecular links (type 4). In such cases, the initial proton transfer may be followed by an intramolecular transfer of the proton, accomplished either by a direct transfer of the proton or by a rotation of the intervening group, to yield a chain which is not reversed in orientation. This is depicted in the sequence 1 to 2 below. Such a process is perhaps less likely to involve a high proton mobility. The intramolecular process, which is now an integral part of the conduction sequence, may require a relatively large energy and is unlikely to occur in a cooperative manner.[90]
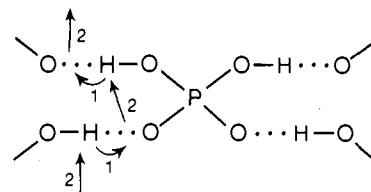
IV. Proton Conduction in Solids

A. Non-Hydrogen-Bonded Systems: Interstitial Migration

1. Materials Lacking Stoichiometric Hydrogen

a. Metallic Oxides

There are essentially two ways in which protons may occur in compounds lacking stoichiometric hydrogen: firstly, by defect equilibria with water and/or hydrogen and, secondly, by electrical injection of protons from ad-

jacent layers. Injection by proton bombardment is also possible but will not be considered here.

Stotz and Wagner[91] have discussed the solubility of water vapor and hydrogen in solid oxides. They assume that the hydrogen is incorporated as an interstitial proton or, under highly reducing conditions with a relatively high concentration of excess electrons, as a hydride ion located in an oxide vacancy where it has an effective charge of +1 relative to the host crystal. For an oxide crystal which contains predominantly anion vacancies ($V_0^{\cdot\cdot}$), in a situation where protons are located interstitially ($H_i^{\cdot}$), they assume the following equilibrium in the presence of water vapor

$$H_2O(g) + V_0^{\cdot\cdot} \rightleftharpoons 2H_i^{\cdot} + O_0$$
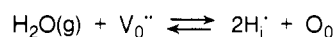
where O_0 denotes an oxygen anion on a normal lattice site. The law of mass action may be applied to this equilibrium, assuming small defect concentrations (to avoid having to consider defect interactions) and yields

$$K_1 = [H_i^{\cdot}]^2 / p_{H_2O}[V_0^{\cdot\cdot}]$$

where p_{H_2O} is the oxygen partial pressure. In a H_2–O_2 mixture the water vapor pressure is controlled by the following process, at sufficiently high temperatures for gas-phase equilibrium to occur, with an equilibrium constant, K_2

$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g)$$
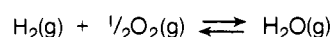
Combination of the two mass action relations yields

$$[H_i^{\cdot}] = K_1^{1/2}K_2^{-1/2}[V_0^{\cdot\cdot}]^{1/2}p_{H_2O}^{1/2}$$

The partial conductivity due to this species is given by

$$\sigma_i = n_i q_i \mu_i$$

where the carriers have charge, q_i, and mobility, μ_i, and exist in concentration n_i. Thus

$$\sigma_{H_i^{\cdot}} \propto [V_0^{\cdot\cdot}]^{1} {}^2 p_{H_2O}^{1/2}$$

For hydride ions, a similar analysis leads to

$$\sigma_{H_0^{\cdot}} \propto [V_0^{\cdot\cdot}]^{1/2} p_{H_2O}^{1/2} p_{O_2}^{-1/2}$$

where the significant difference between these two expressions is the dependence of the latter partial conductivity on $p_{O_2}^{-1/2}$, whereas the former partial conductivity is independent of the oxygen partial pressure.[92] These results clearly are of significance to the application of high-temperature solid-state electrolyte cells for oxygen partial-pressure measurement, for mobile protons will reduce the cell emf below the reversible value attained when only anion vacancies are mobile. Estimates of the limits of interstitial proton concentrations in some oxide systems appear in Table I.

Proton conduction has been examined in a number of oxide systems. In thoria (ThO_2) doped with lanthanides (which yield cation vacancies), studies of the conductivity[92] as a function of the pressures of H_2, H_2O, and O_2 indicate proton conduction at high temperatures and high concentrations of cation vacancies, but low oxygen pressures. Rutile (TiO_2) behaves rather differently because it has an excess of interstitial cations;[93-95] the hydrogen appears to become trapped near trivalent impurities (such as Al^{3+} or Fe^{3+})[96] where it acts as an electron donor to increase the conductivity of the rutile. Most reports on conduction in rutile do not consider any contri-

TABLE I. Limits of Interstitial Proton Concentrations in Some Metal Oxides

Oxide	t, °C	p, atm[a]	Mole fraction of $H_i^{\cdot}$
Cu_2O[b]	900	0.024 (H_2O)[c]	0.6×10^{-6}
	1000	0.024 (H_2O)[c]	2×10^{-6}
CoO[b]	1000	0.024 (H_2O)[c]	18×10^{-6}
NiO[b]	1000	0.024 (H_2O)[d]	2×10^{-6}
ZnO[e]	450	1.0 (H_2)	3×10^{-7}
	700	1.0 (H_2)	1×10^{-5}
TiO_2[f]			Equal to concentration of trivalent impurity

[a] Pressure of gas mentioned in body of table. [b] Data from ref 91. [c] In an oxygen pressure of 7×10^{-4} atm. [d] In an oxygen pressure of 1.0 atm. [e] After ref 91; data from D. G. Thomas and J. Lander, J. Chem. Phys., 25, 1136 (1956). [f] After ref 94.

bution by protons. Experiments with tracers[95a] have, however, confirmed that protons may be injected into the crystal, and a mechanism of electron injection at the cathode together with hole injection at the anode, followed by a rapid proton transfer to the cathode, is invoked to explain the observation that a blue (hydrogen donor) color rapidly appears at the cathode.

Silica (SiO_2), in its various modifications, exhibits a rather similar pattern of behavior to that of rutile, for protons are also found to be trapped at impurity sites in the crystal, and to contribute to the conductivity. A solid-state concentration cell has been used to determine the proton transport number of vitreous silica especially treated to maximize its proton concentration;[96] a proton transport number of 0.58 at 1000° was found, associated with a conductivity of 33×10^{-9} ohm^{-1} cm^{-1}. For single-crystal quartz it has been found[97] that various univalent cations can be conducted through the crystal, but only along the $\langle 0001 \rangle$ channels. The conductivity for lithium (2×10^{-6} ohm^{-1} cm^{-1} at 500°) is orders of magnitude larger than the figure noted above for protons in vitreous silica; this may reflect strong binding of protons at their aluminosilicate sites in the vitreous silica, or a particularly high lithium mobility down the channels in the crystalline quartz. There is some controversy[98] about the nature of the ion charge-carrier, protons or hydroxyl ions, found in certain experiments, but the latter seems unlikely for the goethite (α-FeOOH, correctly formulated) intended, in injecting experiments, to act as hydroxyl source contains only mobile protons and would in any event have decomposed to Fe_2O_3 well below the experimental temperature of 500°.[321] Injection experiments with tritium tracer on thin (6000Å) silica films yield further evidence of proton migration,[99] with an insignificant contribution from sodium ion migration.

Another group of silica-based compounds which should receive mention here is silica gel and related species. In the presence of adsorbed water silica gel has a non-ohmic conductivity which shows several similarities in behavior with that of aqueous solutions. The conductivity is decreased about 1.3 times on substituting D_2O for H_2O, and it is believed from this isotope effect and other evidence that the conductivity is protonic.[100] In the ammonia–silica gel system, where the ammonia adsorbed on the hydroxylated surface of the gel is partially converted to NH_4^+, an ionic conductivity is observed which is attributed to protons.[101,102] Working on a decationated Y Zeolite, Fripiat, et al.,[103,104] also found evidence for a mobile proton from nmr data, but conductivity measurements have not been reported.

The electrical conductivities of a number of other thin oxide films in contact with aqueous solutions have been

reported and their proton conducting properties considered, with reference to aluminum, tantalum, and niobium in particular.[105] The results are somewhat equivocal and no final conclusion can be drawn.

The next oxide to be considered, WO_3, presents some rather interesting contrasts with the previous oxides. WO_3 may be reduced to a hydrogen tungsten bronze, H_xWO_3 ($0 < x < 1$), where the compound has been so-named because of its structural similarity to the sodium tungsten bronzes, Na_xWO_3. H_xWO_3 may be prepared by direct reduction (with Zn and boiling dilute HCl over long periods)[106] or by a catalytic "spillover."[107,108] In the latter method, the WO_3 powder is mixed with a suitable finely divided metal (e.g., Pt black) and placed in a hydrogen atmosphere. The hydrogen is adsorbed on the metal and dissociates into atoms, and the atoms diffuse into the WO_3 particles. The crystal structure of H_xWO_3 has recently been studied by Wiseman and Dickens[459] who suggest that these compounds are more properly formulated as oxyhydroxides, $WO_{3-x}(OH)_x$. This conclusion is in disagreement with that of Sienko and Oesterreicher.[460]

The hydrogen tungsten bronzes have a high, metal-like conductivity, both qualitatively and quantitatively like the sodium tungsten bronzes. On this account, it has been suggested that the hydrogen atoms exist in H_xWO_3 as protons, donating their electrons to the conduction band; i.e., the conduction is taken to be electronic.[106] This view is contradicted, however, by the formulation of the compound as an oxyhydroxide.[459] There is further contradictory evidence, from nmr studies, on the nature of the conducting species. Fripiat, et al.,[103,107] have found that the proton is able to diffuse very rapidly, with a diffusion coefficient of 7×10^{-6} cm^2 sec^{-1} at 298 K and an activation energy of 1.3 kcal mol^{-1}; the results indicate that the protons are still mobile at 80 K. The diffusion coefficient given above is very high, being of the order of that of protons in water. Dickens, et al.,[461] by contrast, find that the protons are immobile below about 250 K, and that the correlation time for proton motion at higher temperatures obeys the approximate relation

$$\tau_c / n\text{sec} = 70e^{-4\text{kcalmol}^{-1}/RT}$$

This result applies for $H_{0.46}WO_3$ and is derived from all of spin–spin, spin–lattice, and rotating-frame relaxation time measurements. A single relaxation process can account for all of Dickens, et al.'s, measurements and also for the concomitant line narrowing observed, so that no special diffusional process is invoked;[461] this result is in conformity with the formulation of H_xWO_3 as an oxyhydroxide.[459] Fripiat, et al.,[107] however, find very different values for spin–spin and spin–lattice relaxation times. The disagreement is ascribed[461] to the different methods of preparation of the samples examined by the two groups, and to their different chemical constitution.

There is no electrical evidence available to support any suggestion of an appreciable protonic contribution to the conductivity, but such a possibility must be considered, particularly if conditions for the manifestation of a high proton diffusion coefficient can be established. There are large numbers of systems which are catalytic to hydrogen exchange, and it would be of considerable interest if the existence of highly mobile protons in some at least of such systems could be proven.

b. Lithium Iodate

Lithium iodate, $LiIO_3$, is capable of dissolving small proportions of HIO_3, which complicate its phase behavior.[109] Nägerl and Haussühl[110] have examined the possi-

bility of injecting proton charge carriers into the pure crystal. They have shown that protons may be injected from hydrogen-saturated palladium electrodes into the (001) face of a $LiIO_3$ crystal, causing an increase of current of 100-fold over the case where the palladium is free of hydrogen; the increase is only threefold when injection into the (00$\bar{1}$) is attempted. The current is also increased (30-fold compared to the hydrogen-free Pd electrode) when the voltage is reversed with the hydrogen-saturated palladium electrode in contact with the (001) face; this unexpected result is explained by the fact that hydrogen dissolved in palladium donates electrons to the palladium, from which they are injected into the $LiIO_3$. With both forward- and reverse-polarity hydrogen-saturated palladium, there is clear evidence of charge injection into the $LiIO_3$, in the appearance of space-charge limited currents at high voltages.

2. Materials without Hydrogen Bonds: Aromatic Hydrocarbons

The earliest work on the conductivity of a simple aromatic hydrocarbon, naphthalene, was interpreted in terms of ion motion,[29e,111] but later work has tended to discount this and discuss the conductivity in exclusively electronic terms because of the general absence of time effects, apart from those which may be due to surface conditions, and because of the presence of photoconductivity closely related to optical absorptions of the materials concerned.[112]

Positive carriers have been noted in anthracene with solution anodes containing strong proton donors, e.g., acids, and this was interpreted as being due to proton injection and conduction.[113] However, further experiments show that the action of the proton donor is to protonate the anthracene surface and form AH^+; proton acceptors, such as oxygen or anthraquinone, in the solution then abstract the proton to form a hole, corresponding to the formation of A^+, which is responsible for the conduction process[114]

$$AH^+ + O_2 \longrightarrow A^+ + HOO\cdot \xrightarrow{AH^-} H_2O_2 + 2A^+$$
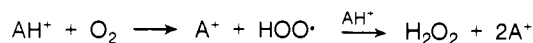
Thus the proton donation is apparently a purely surface effect, rather than the pH-sensitive mechanism of the glass electrode.

B. Hydrogen-Bonded Systems

1. Isolated Hydrogen Bonds and Closed Circuits

No cooperative proton transfer process, as contemplated in section III.B, is possible in materials containing isolated hydrogen bonds, and any discussion of proton conduction in such systems must be couched in terms of an interstitial migration of the ions, from potential minimum to potential minimum.[115] Having no special proton conduction mechanism available, such materials may generally be expected to be poor conductors, with little or no proton contribution to the conductivity. This, indeed, appears to be the situation for the molecular systems discussed below, except when they exist in a high-temperature phase where molecular rotation is facilitated. For the ionic systems containing the bifluoride ion, proton conduction occurs in the low-temperature phase (perhaps because of the reduced energy of ion formation in the ionic environment). At higher temperatures, however, the proton contribution to the conductivity is swamped when the structure becomes "loose" enough to permit migration of the cation (K^+).

a. Small Molecule Carboxylic Acids

The carboxylic acids here considered, of which benzoic acid is the typical example, crystallize in the form of closed dimers[70,71]
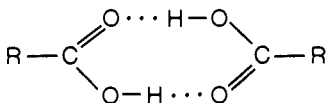
so that the hydrogen bonds are not linked into any form of chain. Definitive dc conductance data for such acids in the form of compressed powders (benzoic, p-toluic, p-aminobenzoic, p-nitrobenzoic, and anisic acids) and of single crystals (benzoic and p-toluic acids) are reported by Eley, Fawcett, and Willis.[116] They found purification to be of considerable importance, as also the absence of all moisture. Dc conductivity decayed over several hours on application of a voltage; the surface conductivity was the major component and decayed most slowly. Ohm's law was not obeyed for the equilibrium current even at low fields. The major result is that a compensation law effect was observed, i.e., log σ_0 and E are linearly dependent on one another.[117-119]

$$\log \sigma_0 = \alpha E + \beta$$

The conductivities of the materials are ascribed to electrons, for the activation energies are high and can be related to the optical absorption process; the compensation effect is ascribed to conduction band bending at the metal electrode–insulator interface (although experimental artifacts may have an influence).[118] Similar results have earlier been reported by Gravatt and Gross[120] for a variety of carboxylic acids[121] in the form of compressed powders; the results are, unfortunately, discussed with reference to molecular structure, and little account is taken of the crystal structures (which are, however, not all known). An earlier paper[122] on the conductivity of a number of hydrogen-bonded carboxylic acids reports much higher conductivities for benzoic acid than now found, but the results are believed[116] to have been distorted by leakage conductance of the cell and, perhaps, surface conductance. Kondo and Oda[123] found little conductivity in pivalic acid (but see below) and concluded that the molecules are dimerized into nonpolar pairs.

The rather clear evidence for electron conduction in these acids using metal electrodes is supplemented, however, by evidence of an injection mechanism with Pd|H electrodes. Using these electrodes, at temperatures above 90°, McKay and Sherwood[124] have found a square-law injection region in the current vs. voltage plot, which decays when currents are allowed to flow for long periods. They infer injection of protons and ascribe the decay to depletion of hydrogen from the Pd|H electrode; this is difficult to conceive for currents of 10^{-11} A unless the experiment was continued for very long periods indeed or, otherwise, unless a part only of the hydrogen is available for injection. However, the possibility of hole injection is not ruled out. McGhie and Sherwood[125] have also investigated the self-diffusion of $C_6H_5{}^{14}COOH$ and of $C_6H_5COO^3H$ in single crystals of benzoic acid. A different diffusion rate is obtained for the two tracers, which might imply a separate proton transfer process, but it is concluded, on the basis of the influence of water vapor and consideration of the molecular form and packing in the crystal, that the difference is due to an extrinsic tritium diffusion process arising from exchange of the tritium with included water, coupled with interstitial diffusion of the water molecule; i.e., a free proton diffusion process is not accepted.

Tetrolic acid, 2-butynoic acid ($CH_3C{\equiv}COOH$), has a structure[126] in which the carboxylic groups are linked in a chain by hydrogen bonds. Attempts to inject protons[127] with a Pd|H electrode into powders and into single crystals in a direction approximately normal to that of the hydrogen-bond chain failed, since the conductivity was ohmic up to 10 kV cm^{-1}.

Pivalic acid, $(CH_3)_3CCOOH$ (2,2-dimethylpropanoic acid), also has a structure[128] based upon dimerization[123] of the molecules into closed pairs; however, at temperatures greater than 280 K it exists in a plastic, rotator phase. Self-diffusion measurements of labile protons, using $(CH_3)_3CCOO^3H$ as the tracer, yield a fast proton transfer with a diffusion coefficient[129]

$$D \text{ cm}^2 \text{ sec}^{-1} = 2.3e^{-8.5 \text{kcal mol}^{-1}/RT}$$

whereas the molecular diffusion process is some hundred times slower; a similar distinction between the two processes is indicated by an analysis of the narrowing of the appropriate nmr lines with temperature. The results are believed to be intrinsic, and not due to the presence of water, because deliberate addition of water alters the details of the observed behavior. Dc conductivity measurements[129] using a guard ring electrode yield a very different activation energy, 35 kcal mol^{-1}, with indications of space-charge injection from a Pd|H electrode. The injection behavior is regarded as being indicative of proton injection, but not conclusive proof thereof.

Mechanisms for diffusion and for conduction based upon switching of single molecules among the 12 alternative dimer positions are postulated; the diffusion process is conceived to operate by an exchange process following a rotation, while conduction may arise from interstitial proton migration or from exchange by rotation of single molecules with, alternately, one extra proton and a deficiency of one proton. The latter process would require cooperative proton transfers within a dimer before the rotations of the molecules.

b. Hydroxy Compounds

i. Orthoboric Acid. Orthoboric acid, H_3BO_3, has a structure[13,130] consisting of $B(OH)_3$ groups each hydrogen-bonded by three pairs of bonds to form a layer structure, thus accounting for the perfect basal cleavage. Although the structure could be pictured as of type 4, with chains of hydrogen bonds broken by intramolecular links, it seems more appropriate to note the closed circuits of directly linked bonds and place it within type 3. The dielectric properties arise essentially from adsorbed water.[131,217] Electrolysis of powders yielded no hydrogen gas, and the current was constant, independent of time.[131] Bradley, Munro, and Ali[132] report on the dc conductivity of orthoboric acid powders as a function of both temperature and pressure. The conductivity is low ($\sigma = 6 \times 10^{-9}$ ohm^{-1} cm^{-1}) with small activation energy to about 210°; when there is a large discontinuity which is attributed to a phase change. There is, in fact, quite a complex phase behavior which is not fully elucidated. Bradley, et al., assume that orthoboric acid is a proton conductor, but the dielectric and electrolysis results do not support this supposition.

ii. Pentaerythritol. Pentaerythritol, 2,2-bis(hydroxymethyl)-1,3-propanediol ($C(CH_2OH)_4$), has a room-temperature-stable tetragonal layer-structure which contains an infinite two-dimensional network of hydrogen bonds, each molecule being attached to four others in the plane.[133] This phase undergoes a first-order transformation at 458 K to a face-centered-cubic, plastic structure which re-

sults in a major, though incomplete, destruction of the hydrogen-bond network.[134,135] Much of the physical data on pentaerythritol, except the electric data (below), are summarized by Smith.[136] In the low-temperature phase there is no appreciable dielectric dispersion, but there is a slight anisotropy of the dielectric constant, with a value of 2.9 normal to the hydrogen-bonded plane and 3.7 parallel to it; these values of the dielectric constant are almost temperature independent.[137,217] However, on heating the crystal through the transition point, there is a dramatic increase in permittivity and loss, with indications that the low-frequency capacitance and loss was increased by space-charge accumulation when "blocking" electrodes of metal foils attached with vaseline were used.[137] The dc conductivity, measured without a guard ring on specimens dried at 110°, was exceptionally high at 6.4×10^{-6} ohm^{-1} cm^{-1} at 200° and with an activation energy of 20 kcal mol^{-1}; there are some indications of a decay of the currents with time. This activation energy is close to the enthalpy of sublimation of pentaerythritol in the high-temperature phase, suggesting that freedom for molecular movement is required in the conduction process. By nmr,[136] the activation energy for rotation is 23 kcal mol^{-1} while that for self-diffusion is 24 kcal mol^{-1}, both in the low-temperature phase; these may be expected to be lower in the plastic phase and thus not inconsistent with the above hypothesis concerning the conductivity. Kiriyama, et al.,[137] propose that the conductivity in the high-temperature phase must thus be due to "a kind of protonic transfer."

More recent measurements,[127,138] conducted in the low-temperature phase only, apparently in anticipation of premonitory effects near the transition point, show an anisotropy of the surface dc conductivity[138] and activation energies of about 20 kcal mol^{-1} above 400 K, a temperature associated with the liberation of traces of water from the surface. The bulk conductivity[127] of a solution-grown single crystal has an activation energy of 23 kcal mol^{-1} along the c direction, but a vapor-grown crystal has an activation energy for conduction in the same direction of 60 kcal mol^{-1} (there is some confusion between the text and the figure to which it refers). The difference is ascribed to a reduced water content in the vapor-grown crystal. Attempts to obtain space-charge injection effects with Pd|H electrodes failed.[127]

It thus appears that the low-temperature phase is non-proton conducting, but there is evidence to suggest that the high-temperature plastic phase may well be proton conducting; it would be useful for injection experiments to be performed on the latter phase.

iii. Sugars. The crystal structure of sucrose[487] is rather rigid and contains molecules held together by six hydrogen bonds parallel to the (100) plane and only one out of the plane. There is a cleavage parallel to the (100) plane.

The electrical conductivity of sucrose[488] has ionic characteristics, i.e. it decays slowly with time, and is described by a two-term equation, such as the following for the [100]·sin β direction

$$\sigma = \sigma_{0_1} e^{-16.5 \text{kcal mol}^{-1}/RT} + \sigma_{0_2} e^{-10.0 \text{kcal mol}^{-1}/RT}$$

where the activation energies are in the expected range for an ionic conductor. At the same time, it is known that water impurity is accommodated along dislocations, in essentially cylindrical columns, emerging at (100) faces. Protonic conductivity along these dislocations was tested for by using Au and Pd|H electrodes in a guarded electrode system. When the palladium had been saturated electrolytically with hydrogen, it was found that the conductivity increased by three orders of magnitude over the

value found with the inert electrodes, without a significant change in the activation energy; the behavior was interpreted as arising from proton injection and transfer along the water-filled dislocations. This result is taken as a warning that similar effects can occur in other crystals prepared from protonic solvents. Furthermore, it should be noted, such paths in single crystals provide a mechanism for nonbulk conduction which will by-pass a guard-ring, and may invalidate single-crystal measurements in certain situations.

The electrical[489] and dielectric[490] properties of some sugars, hydrated and dehydrated (also of cellulose and starch), have been measured. Absorptions are observed in dehydrated material crystallized from the melt at about 1 MHz at 20°, but little absorpion is observed in the crystalline material; the absorptions disappear on benzoylation of the hydroxyl groups. The absorption is thus ascribed to rotation of hydroxyl groups.

c. Alkali Metal Bifluorides, Especially KHF₂

The properties of the alkali metal bifluorides, MHF₂, have been summarized by Bruinink.[139] These materials contain cations, M$^+$, and strongly hydrogen-bonded linear anions, FHF$^-$, each isolated from the other. Potassium, rubidium, and cesium bifluorides have a low-temperature (α) tetragonal phase in which there are alternating layers of ordered FHF$^-$ ions and of cations, with the layers normal to the unique c axis; in the high-temperature (β) cubic phase the ions are believed to be similarly arranged but the anions are lined up randomly along the four body diagonals of the cube (K and Rb) or along the three cubic axes (Cs).[13,140,141]

The ac conductivities of pressed powder pellets of all of these materials have been surveyed[139] and were found to exhibit similar frequency dependent conductivities (see below), yielding kinked linear plots of log $\sigma(0)$ vs. $1/T$, where $\sigma(0)$ is the ac conductivity extrapolated to zero frequency. Furthermore, these plots show large stepwise increases in conductivity (about one to two orders of magnitude) at the known transition temperatures. While the slopes have large differences among them in the low-temperature α-phase region (23 to 31 kcal mol^{-1}), there is similarity in the high-temperature β-phase region (ca. 20 kcal mol^{-1}). These results suggest a general similarity in conduction behavior among the alkali metal bifluorides; detailed information on that behavior is provided by the very extensive measurements which have been reported on one of these bifluorides, KHF₂.

Conduction measurements on KHF₂ were first reported by Davis and Westrum[142] whose results conform with those reported above. These measurements were considerably extended by Pollock and Sharan,[143] who also attempted to identify the charge-carriers by electrolysis and by comparing the ac conductivity of KHF₂ with that of its deuterated analog, KDF₂, both in the form of powdered pellets. These results, too, were similar to those reported above, with activation energies of 15.6 kcal mol^{-1} in the α-phase and 18.7 kcal mol^{-1} in the β-phase (values corrected by Bruinink and Broers[144]). The activation energies for KDF₂ are about 2 kcal mol^{-1} greater for each phase than for the corresponding phase of KHF₂. The conduction was attributed to interstitial proton migration, most of the activation energy being utilized in defect formation.

More detailed and extensive measurements have been reported by Bruinink and coworkers, in an excellent series of papers.[1,144,145] Bruinink and Broers[144] performed ac and dc conductivity measurements on single crystals and compressed powder pellets of KHF₂ using platinum

point electrodes under vacuum and in an HF atmosphere created by heating excess powdered KHF_2; in the slight excess pressure of HF obtained as described, where the decomposition of the KHF_2 sample was inhibited, the results were reproducible. The ac behavior was explicable in terms of an equivalent circuit consisting of a parallel combination of a constant conductance, $G(0)$, a constant capacitance, $C(\omega)$, and a Warburg admittance

$$Y(\omega) = (1 + j)k\omega^{1/2}$$

where the Warburg admittance[46,146] may be represented by distributed series resistance with parallel capacitance. The conductance and capacitance were shown to be true bulk properties by variation of sample size. The Warburg admittance is ascribed to microscopic inhomogeneities by Bruinink and Broers,[144] but Mitoff and Charles,[35] in discussing the admittance observed in other ion conductors, ascribe such observations to electrochemical action at electrodes.

The ac conductivities of powdered pellets and of single crystals are rather similar in the β-phase, but in the α-phase the powder conductivity is much higher than that of single crystals due, it is believed, to surface conduction. The single crystal conductivity is isotropic which, in view of the strong layering in the crystal, is perhaps surprising. The following activation energies are reported: single-crystal (α-phase) 17 kcal mol^{-1}, (β-phase) 20.5 kcal mol^{-1}; powder (α-phase) 29–31 kcal mol^{-1}, (β-phase) 19.7 kcal mol^{-1}. The dc conductivities display some polarization and differ in value from the extrapolated ac conductivity $\sigma(0)$, but this difference disappears in a hydrogen atmosphere for the α-phase, suggesting that protons are indeed the charge-carriers in that phase.

Definitive experiments to establish the charge-carriers and their transport numbers are reported by Bruinink and Kosmeijer[145] who have performed determinations of the emf developed across KHF_2 in a hydrogen gas concentration cell, and of the matter transport in a Hittorf–Tubandt type of experiment.[25] Reversible, porous electrodes were successfully prepared either from a platinum support covered with a layer of platinum black or from platinum-activated carbon. The electronic contribution to the charge-transfer process was found to be negligibly small.

The nature of the ions involved in conduction in the better conducting β-phase was determined by passing current through a set of three powder pellets pressed together in a hydrogen atmosphere. At 210°, it was found that $t_K = 0.25 \pm 0.05$, $t_F = 0.75 \pm 0.05$, and $t_H \approx 0$ (β-phase).[491] On account of the small temperature range of stability of the β-phase, no temperature dependence could be determined. Electrolysis under vacuum did not yield usable results because voluminous reaction products were formed, particularly at the anode.

The conductivity of the α-phase is too low for matter transport to be detected in reasonable times, and powder pellets conduct preponderantly by a surface mechanism, in contrast to the situation in the β-phase. However, the dc conductivity of single crystals in the α-phase with active hydrogen electrodes in a hydrogen atmosphere showed no polarization effects, in contrast with the observations under vacuum and for the β-phase in hydrogen; for the latter this may be related to the nonzero values of t_K and t_F. Hence, as before,[142] protons are taken to be the bulk of the charge-carriers in the α-phase. The low conductivity of the α-phase is ascribed to the high charge density of the proton and the likelihood of a free proton forming hydrogen bonds which will inhibit its further movement.

Bradley, et al.,[132] have measured the ac conductivity

of KHF_2 at pressures up to 60 kbars and 350°. The phase transition discontinuity was observed as at atmospheric pressure and, from the variation of the activation energy with pressure for the α-phase, an activation volume of 2.5 cm^3 mol^{-1} was calculated; no such value could be determined for the β-phase on account of its decomposition. This activation volume is small for a typical solid forming a Frenkel defect ($V = 11.55$ cm^3 mol^{-1} for AgCl[147]), and this is ascribed to an extension of the $F^- \cdots F^-$ distance on the removal of a proton partly offset by the contraction which may occur around the interstitial proton.

2. Materials with Chains of Hydrogen Bonds, Broken by Intramolecular Links

This class of hydrogen bonded materials is comprised of a large variety of materials of different chemical classes and structures. It has been subdivided as follows: (a) salts containing no acid protons; (b) acid salts; (c) acids; (d) miscellaneous hydrates; (e) hydrogen-bonded molecular species (e.g., imidazole). Examination of the experimental data reveals that there are indications of proton conductivity in a number of these subdivisions. Thus, there is at least a partial proton conductivity in the ammonium salts when the ammonium ions are free to rotate, but the structures seem generally "loose" enough to permit motion of the ammonium ion as a unit, rather than force the ion to undergo a reconstruction process. The oxonium ion, on the other hand, can transfer its "allegiance" to a pair of protons, gaining one and losing another so that the net result is a rotation, without undergoing significant reconstruction; thus, proton migration in a suitably bonded oxonium salt may be easy. The acid salts considered are mostly ferroelectric at low temperatures, with the protons in ordered arrangements, but converting to proton-disordered, paraelectric states at higher temperatures. In such materials there is clear evidence of a degree of proton tunnelling across the hydrogen bond and, when this is associated with group rotation, conduction can occur. The class of order–disorder hydrogen-bonded ferroelectrics constitutes a large, well-characterized group of materials among which proton conductors may be expected to be discovered; this reviewer, in fact, "re-discovered" a number of ferroelectrics during the literature search for the review, simply from their proton-conducting characteristic. It must be noted, however, that the class of proton conductors is broader than the class of ferroelectrics, for only materials which have structures with a unique polar axis (this occurs in 10 of the 32 crystal classes) may be ferroelectric, and there is the further phenomenological requirement that the direction of polarization be reversible by the application of an electric field, without causing electric breakdown of the solid.[19,173] These limitations will not, of course, apply to proton conductors.

The acids described have rigid structures, with no group-rotations evident, and proton conduction appears to be generally absent (except, perhaps, when a high field is applied). The hydrates are a large class of materials whose conductivity has been examined in detail for a few materials only; the present group may not be fully representative of hydrates in which chains of hydrogen bonds can be perceived, and it is difficult to draw general conclusions at this stage. The last group, involving compounds such as imidazole and urea, is of especial interest because of its biological relevance; there are clear indications of considerable proton conduction in these materials.

a. Salts Containing No Acid Protons

The conductivities of ammonium salts which contain no acid protons have been examined in a number of cases; among these the conductivity is best characterized in ammonium chloride, while other significant studies have been performed on ammonium nitrate and ammonium sulfate. A good deal of attention has been focused on ammonium perchlorate because of the possible influence of proton motion in the important thermal decomposition process. This thermal decomposition does, however, make interpretation more difficult. A recent determination yields a very high conductivity for oxonium perchlorate, suggesting that the conduction proceeds *via* a chain of proton transfers.[470]

The first measurements of electrical conductivity on the ammonium halides were reported by Herrington and Staveley[148] who studied the conductivities of single crystals of pure and doped NH_4Cl (and of CsCl and KCl) in some detail and, rather less thoroughly, ammonium and potassium bromides and iodides, tetramethylammonium iodide, ammonium and potassium stannichlorides, and ammonium and rubidium fluorophosphates.

i. Ammonium Chloride. The conductivity of single crystals of ammonium chloride in its CsCl structure[13,149] (184.3 to $-30.5°$) has been examined by a number of workers;[148,150,151,164] the activation energy is 26.5 kcal mol^{-1} by a dc method,[148] and 29 kcal mol^{-1} by an ac method[151] (frequency not stated). On doping with a divalent cation, the ac activation energy drops to 3.5 kcal mol^{-1}, which is ascribed to the charge-carrier migration energy, yielding an energy of formation of Schottky pairs of 51 kcal mol^{-1}. The conductivity of NH_4Cl is about 1.3 times that of ND_4Cl in the high-temperature intrinsic region, although the activation energies are similar. This suggests that the rate-determining step in the conduction process is the frequency of attack of the proton (or deuteron) on a potential barrier.[151]

The Herrington–Staveley[148] model for the conduction process is based on the supposition that there is a significant proportion of dissociation in the crystal to form molecular species

$$NH_4^+ + Cl^- \longrightarrow NH_3 + HCl$$
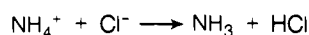
Assuming the conduction to be ionic, and not electronic, the following mechanism is then suggested:[151] (1) a proton switch from the NH_4^+ ion to a Cl^- adjacent to a vacancy, corresponding to the chemical equation above; (2) migration of either of these molecules into the vacancy; (3) a reversal of the proton switch, to re-form NH_4^+ and Cl^-.

Experiments aimed at positively identifying the charge carriers, by electrolysis[164] and by concentration cell emf measurements, are somewhat equivocal.[150] The electrolysis experiments yield hydrogen in the proportions expected for proton conduction, when a proton-injecting anode of $NH_4H_2PO_4$ is used. The emf measurements, however, indicate that there is a significant electronic contribution to the conductivity (an electron transport number of about 0.2) at high hydrogen pressures, but that this drops to zero at low hydrogen pressures. The proton transport number is (very roughly) one-third of the total ion transport number. These results are somewhat vitiated by the fact that it was not possible to establish true thermodynamic equilibrium between the gas phase and the crystal samples.[150]

Most of these experiments were performed on crystals grown from solutions containing urea, to suppress dendrite formation. Although no urea impurity could be de-

tected by nmr and ir absorption[151] techniques, electrically significant quantities may be present since the urea must be adsorbed to control the crystal habit. Urea has recently been observed to participate in proton conduction,[283] so that investigation of the role of urea in the conduction process in NH_4Cl is required.

ii. Ammonium Nitrate. Ammonium nitrate has a very complex phase behavior,[152] associated with the fact that both ions may be fixed in the crystal, or may rotate. In all, seven different phases are observed, five of which commonly occur (from the low-temperature phase VII, through V, IV, and II to the high-temperature, plastic phase I). Phase III is observed (between IV and II) on heating and is observed only in the presence of moisture or after repeated thermal cycling on cooling. These properties suggest that ammonium nitrate may behave in some respects like a plastic, molecular crystal.

The conductivities of the phases are generally rather low, except for phase I, with an activation energy[153] of 16.0 kcal mol^{-1} compared[154] with 22.4 kcal mol^{-1} for phase II. The activation energies for NH_4^+ diffusion in phase II, measured by nmr relaxation techniques,[154] are in close agreement with those for electrical conductivity, as also are the diffusion coefficients calculated from the nmr diffusion correlation time, and from the conductivity using the Einstein relation. This implies that NH_4^+ diffusion is solely responsible for the electrical conductivity, with no separate contribution from proton transfer on the Herrington and Staveley[148] model. Similarly, for phase I, there is general agreement between conductivity and nmr relaxation times, suggesting again that NH_4^+ diffusion satisfactorily accounts for the conduction.[154] Two discrepancies occur, however, in the data for phase I. Firstly, the nmr diffusion coefficient based on line-width measurements is two orders of magnitude lower than that based on relaxation times, and, secondly, the conductivity data show an increased slope in the higher temperature region. This may imply two conduction mechanisms, only one of which has been taken into account in the above analysis.

Dielectric measurements[155] on phases I to III yield rather discrepant results from those for the conduction and nmr experiments described above. For example, in phase II the activation energy for dielectric relaxation is 104 kcal mol^{-1} while that for the nmr relaxation is only 24.3 kcal mol^{-1}. The dielectric absorption is ascribed to the motion of dipolar pairs of ions, $H_3NH^+–ONO_2^-$, hydrogen-bonded to each other, which need not be involved in the dc conductivity or nmr relaxation. It is thus not possible to draw any definite conclusions as to the charge-carriers, but it would appear that the "plastic" phases permit the ammonium ions to diffuse quite readily.

iii. Ammonium Sulfate. Ammonium sulfate, $(NH_4)_2SO_4$, is ferroelectric[13,19] below 223 K $(-49°)$; however, the transition is not of the order–disorder type but is displacive, as a result of changes of the hydrogen bonding structure.

The dc conductivity of single crystals has been measured by Schmidt[156] in the *b* direction, using a guarded silver-paint electrode, over the temperature range -72 to $+200°$. The conductivity was found to be ohmic, but a small polarization effect was found on first application of a field to a sample; conductivities were apparently measured after the decay of this polarization, but this is not stated explicitly. The crystals tend to crack when passing through the ferroelectric transition, and there are fluctuations in conductivity at the transition. The conductivity from -48 to $+200°$ is given by

$$\sigma/\text{ohm}^{-1}\,\text{cm}^{-1} = 29e^{-17.6\text{kcal mol}^{-1}/RT}$$

This activation energy is much larger than that for NH_4^+ rotation as determined by nmr[13,157] which has an activation energy of about 2 kcal mol^{-1}. Therefore, it is suggested that the conductivity is not governed by NH_4^+ rotation. This may imply that the conduction (if it is protonic) is limited either by the rate of sulfate rotation or proceeds by an interstitial mechanism. Assuming that from one to eight of the eight nonequivalent protons are participating in the proton conduction, a mobility at infinite temperature is calculated.[156]

$$2.8 \times 10^{-3}\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1} < \mu_0 < 2.2 \times 10^{-2}\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$$

iv. Ammonium Perchlorate. Particular interest in the electrical conductivity of ammonium perchlorate has been generated by the suggestion that a charge-transfer step occurs in the decomposition of this thermally labile material,[158] and, consequently, the results of a rather large number of investigations have appeared.[159-170] Nmr,[171,172] cold neutron scattering,[462,463] and many other[464] experiments indicate a low rotational barrier to the NH_4^+ ion rotation,[465] while the ClO_4^- ion only undergoes free rotation after an orthorhombic–cubic transformation at 240°.[158]

A number of the reports[159-164] describe experiments with generally simple and reasonably reproducible results. Such experiments were performed on compressed powders[159,160] and on single crystals generally with dc but occasionally[160] with low-frequency ac. These workers report straight-line plots of log σ against $1/T$, yielding activation energies of about 21–32 kcal mol^{-1} for the powder pellets, rather dependent on the atmosphere; the conductivity and activation energy increased significantly in an ammonia atmosphere.[160] Electrolysis of compressed pellets and single crystals of ammonium perchlorate using $NH_4H_2PO_4$ as proton-injecting anode produces hydrogen in the proportions expected for pure proton conduction.[164] For single crystals, Wise[160] reports conductivity results identical with those for pellets, whereas Maycock, et al.,[161] describe a more complex result, with kinks in the log σ vs. $1/T$ plot at a number of points, with one of particular note at 255° corresponding approximately to the orthorhombic (low temperature) to cubic (high temperature) transformation. Polarization phenomena were observed in this investigation below 125°. The consensus was that proton transport was implicated in the conductivity, based on the effect of ammonia atmosphere,[160] the observation of hydrogen gas evolution,[162-164] and the relationship between the conductivity and the rate of decomposition.[161] The generally transparent appearance of a crystal (except near the positive electrode) when subjected to temperatures near 280° while under the influence of an electric field, compared to the opacity of crystals subjected to the same temperature treatment in the absence of an electric field, seemed clear evidence of migration of cation vacancies to the anode where the proton transfer preceding decomposition is facilitated.[161] Electron conduction was proposed, however, for the temperature range 280–350°.

A theoretical analysis of the electrical conductivity of ammonium perchlorate has recently appeared.[464] The model used was that of polarizable point ions, and was investigated by a computer simulation technique. The ions considered were NH_4^+ and ClO_4^-, and no account was taken of the possible formation of protons. The energies of a large variety of different defect types were calculated: a Schottky defect pair was found to have the smallest formation energy, at 38 kcal mol^{-1}, compared

with 93 kcal mol^{-1} for a Frenkel pair. Accordingly, interstitial NH_4^+ ion conductance was regarded as negligible. The activation energy for migration of an NH_4^+ vacancy in the $\langle 110 \rangle$ direction was found to be 104 kcal mol^{-1}; this requires a comparison with experimental results under thermodynamic equilibrium conditions, that is, at high temperatures. However, the experimental activation energy of Maycock and Pai Verneker[161] is 56 kcal mol^{-1} from 255 to 280°, and 129 kcal mol^{-1} from 280 to 350°. Therefore, there is a discrepancy between the experiment and theory which implies that the ions cannot be treated as structureless spheres. A low activation energy "turnstile" mechanism of NH_4^+ ion migration through a pair of slowly rotating adjacent ClO_4^- ions is therefore proposed for the 255–280° temperature range.

No account is taken in this model of possible hydrogen bonding interactions, and the special "turnstile" process has had to be invoked to obtain agreement between the theory for this model and experiment. Furthermore, as noted, it has been necessary to postulate thermal equilibrium in the crystal in just that temperature region where decomposition is occurring. For these reasons, as well as for the reason that the conductivity data are, in fact, much more complex than has been contemplated in the analysis (see below), the model proposed can only be regarded as a first step toward a more comprehensive analysis.

More recent observations[165-167,169,170] have complicated the simple picture of the conductance considerably. As already mentioned, ammonium perchlorate is thermally labile, but the studies reported above were not concerned with the consequences of the thermal decomposition on the conductivity. Thus, although Maycock, et al.,[161] relate the conductivity to the thermal decomposition as a function of time, their plots of log (σT) vs. $1/T$ give no indication of a time variation of the conductivity (either through decomposition or polarization) nor of the reproducibility of the data, especially as the results were obtained using increasing temperatures so that the material at the final high temperatures will have been partially decomposed.

Jacobs and coworkers[165-167] report repeated runs of ac conductivity measurements as function of temperature, also with increasing temperature, with material which had been degassed for at least 16 hr under vacuum (10^{-6} mm). Results determined with and without guard rings were similar; thus surface conductance is not significant. On the basis of experiments with various atmospheres, thermal cycling, and doping with Ba^{2+}, Jacobs and Ng[167] suggest a mechanism of formation of proton defects (NH_3 molecules at cation lattice sites) followed by migration of those defects in the bulk by transfer of protons from adjacent ammonium ions. The activation energy for the proton migration is suggested to be very small.

A considerably different view of the conductivity of ammonium perchlorate is taken by Thomas and coworkers.[169,170] In an attempt to examine the proton contribution to the conductivity, they have compared the dc and step-voltage transient currents (using earthed guard rings) through dried single crystals of ammonium perchlorate and of the structurally almost identical rubidium perchlorate.[169] They find little difference between these materials, either in absolute values of their conductivities at high temperatures or in their activation energies for conduction (about 25 kcal mol^{-1}); the experiments were performed commencing at the highest temperature (about 160°) and reducing the temperature. The minimal differences seem to suggest that no special proton trans-

fer process is operative but that the ion transfer mechanism involves NH_4^+ ions as a unit.

These conductance measurements have been extended in an elaborate study[170,466] of the effects of varying the ambient atmosphere and the dc field. In general, the results are rather similar to those found by Jacobs and coworkers, with the surface conductivity increasing exponentially with ammonia and with water vapor pressure, and with the ohmic behavior at low fields changing to increasing conductivities at higher fields. Log (σT) vs. $1/T$ plots for single crystals show the characteristic kinked linear plot attributed to the extrinsic and intrinsic conduction regions, while for compressed powder pellets only one slope is obtained, that characteristic of the high-temperature, intrinsic region (activation energy 25 kcal mol^{-1}). From this, and the comparison with rubidium and potassium perchlorates, already mentioned, it is concluded that the conduction has an ionic component. However, the non-ohmic behavior is attributed to an electronic mechanism perhaps occasioned by a charge injection process. It is argued that the conductivity increase on water or ammonia adsorption is not unequivocal evidence of a proton transfer conduction mechanism, but it is conceded that, at sufficiently high surface coverage, a proton charge-transfer process may occur. This will require detailed adsorption studies to elucidate the mechanism further.

The rather unsatisfactory state of knowledge with respect to the conductivity of ammonium perchlorate is perhaps understandable when the considerable experimentation which has gone to establish the conduction behavior in the thermally stable alkali halides is recalled; it will not be surprising if an even greater accumulation of experimental knowledge is required for the thermally labile ammonium perchlorate. Thus, for the purposes of this review, the conduction results on ammonium perchlorate must serve as a warning of the great experimental care which needs to be exercised, rather than as an example on which detailed interpretations may be based.

v. Oxonium Perchlorate. Oxonium perchlorate, $H_3O^+ClO_4^-$, has a crystal structure which, by analogy with the structure of ammonium perchlorate, was early recognized[467] to contain the oxonium (or hydronium) ion, H_3O^+. There are two modifications of the crystal structure,[13] a monoclinic form[468] stable below about $-30°$ and a related orthorhombic form[469] stable to the melting point of 49.6°. In the low-temperature form the tetrahedral oxonium and the pyramidal perchlorate ions are arranged in hydrogen-bonded sheets, in such a manner that each oxonium ion is hydrogen-bonded to three different perchlorate ions. The high-temperature form has been proposed[467] to have the H_3O^+ disordered or tumbling among two or more different orientations; the latter is confirmed by the observation by cold neutron scattering[462] that the H_3O^+ undergoes a hindered rotation with a torsional frequency of 497 cm^{-1} and with a barrier to rotation of 1.8 kcal mol^{-1}. The extensive hydrogen bonding, similar to that in ammonium perchlorate, and the disorder in the high temperature phase suggest that oxonium perchlorate in this phase is a good subject for proton conduction studies.

Ac electrical conduction and diffusion experiments have recently been undertaken by Potier and Rousselet.[470] Single crystals were not grown and the experiments were conducted with compressed powder disks. The conductivity was measured at frequencies from 35 to 5000 Hz, but it is not made clear what frequency was used in the various circumstances; no effect of changing frequency is considered. Measurements were made with

decreasing temperature and yielded an order of magnitude decrease in the conductivity on passing through the phase transition, at $-24°$. The conductivity behaved as follows:

$$\sigma/\text{ohm}^{-1}\,\text{cm}^{-1} = 490e^{-8.5\text{kcal mol}^{-1}/RT} \qquad -10° < t < 48°$$

$$\sigma/\text{ohm}^{-1}\,\text{cm}^{-1} = 3.2e^{-5.6\text{kcal mol}^{-1}/RT} \qquad -24° < t < -10°$$

$$\sigma/\text{ohm}^{-1}\,\text{cm}^{-1} = 4.6e^{-6.8\text{kcal mol}^{-1}/RT} \qquad -55° < t < -24°$$

The first expression describes the conductivity in the intrinsic conduction region, the second is interpreted as extrinsic and is ascribed to the effects of crystal contacts, while the last again describes intrinsic conductivity but in the low-temperature form. The diffusion of tritons in the compressed powder was found to proceed with an activation energy of 8.3 kcal mol^{-1} near room temperature, and with a diffusion coefficient of 1.60×10^{-9} cm^2 sec^{-1} at 25°, while ^{18}O diffusion was about three orders of magnitude slower. There is evidence that ClO_4^- ions diffuse very slowly indeed, and there is little or no oxygen exchange with these ions,[470] so that the oxygen diffusion arises from H_3O^+ movement. The triton has, then, an additional independent diffusion mechanism or, perhaps, there is a complex diffusion mechanism in which the triton diffuses independently in the rate-determining step. The triton diffusivity is found to correlate with the intrinsic conductivity, using the Nernst–Einstein relation (note the similar activation energies of about 8.4 kcal mol^{-1}). The fact that the correlation coefficient is about 0.74 is taken to suggest that the conduction mechanism is one involving proton defects; this argument is weakened, however, by the fact that a triton diffusivity is being compared with a (presumably) proton conductivity.

A conduction mechanism derived from that of Wise for ammonium perchlorate[160] and of Eigen, et al.,[387] for ice is proposed. This mechanism involves a Grotthus-type "handing-on" procedure from ion to ion for the proton, which moves from bond to bond by molecular rotations.

While the general pattern of the results is readily acceptable, the effect of frequency on the conductivity needs to be clarified; in the case of KH_2PO_4 (see section IV.B.2.b, below), the ac conductivity is some three orders of magnitude higher than the corresponding dc conductivity. Furthermore, since the method of preparation of the oxonium perchlorate involves addition of water to perchloric acid at low temperatures, there is considerable danger of water contamination, and one would wish to know how the conductivity is affected by small changes in the water content of the sample.

vi. Triglycine Sulfate (TGS). Triglycine sulfate (TGS), $(C_2H_5NO_2)_3 \cdot H_2SO_4$, is ferroelectric below 47° and paraelectric at higher temperatures, both structures being monoclinic.[19] Two of the glycine residues are believed to be protonated glycinium ions while the third is a normal zwitterion,[471,472] and there is an intricate network of hydrogen bonds holding the sulfate ions and glycine residues together. The structural transformation is probably of the order–disorder type.

The conductivity has been investigated from room temperature to 80°, through the transformation.[473a] In the ferroelectric phase, the conductivity of a single crystal along the ferroelectric axis is given by the relation

$$\sigma/\text{ohm}^{-1}\,\text{cm}^{-1} = 10^8e^{-29\text{kcal mol}^{-1}/RT}$$

while in the paraelectric phase, the following relation holds.

$$\sigma/\text{ohm}^{-1}\,\text{cm}^{-1} = 0.5e^{-19\text{kcal mol}^{-1}/RT}$$

No details of the conductivity measurement procedures are given. These activation energies are very much less than the width of the forbidden band (116 kcal mol^{-1}), as determined from the wavelength of the optical absorption edge. On account of this difference, the conductivity is regarded as certainly ionic, with the activation energy being ascribed to the sum of the energies of defect formation and migration. Photoelectric experiments demonstrate that it is possible to inject electrons from a gold contact into the TGS crystal.

Gurevich, et al.,[20,473b] also report on the dc conductivity of TGS single crystals, measured by a guarded electrode system in various directions. The conductivity in the unique direction is 1.5 orders of magnitude greater than in directions normal thereto.[20] The conductivity reported is, however, some two orders of magnitude larger than that reported by Royal, et al.[473a] (and with a lower activation energy, about 19 kcal mol^{-1} in the ferroelectric phase). Gurevich ascribes his measured conductivities to an impurity mechanism since they are much larger than would be expected on a simple intrinsic proton conduction mechanism. He mentions an unpublished observation of gas (presumably hydrogen) evolution during the passage of a current through TGS and concludes that the intrinsic conduction mechanism possibly proceeds by proton "hole" transfer, with the rather high mobility of 2.5 × 10^{-2} cm^2 V^{-1} sec^{-1}.

Experiments in the presence of water vapor[474] show that the conductivity of a TGS crystal increases with increasing humidity. Since it is observed that water vapor is physically adsorbed on TGS throughout the temperature and humidity range observed, it is concluded that the conductivity effects observed arise from adsorption of water on the fracture surfaces of the TGS crystals.

vii. Uronium Nitrate. Uronium (or urea) nitrate, $(NH_2)_2COH^+NO_3^-$, has an extensively hydrogen-bonded layer structure[475] containing planar uronium and nitrate ions alternating with one another within a layer. The electrical conductivity[476] in the solid state is high (2 × 10^{-7} ohm^{-1} cm^{-1} at 60° and 50 Hz, for a powder pellet), and transport measurements indicate depletion of protons at the anode, with a proton transport number of unity. The activation energy is 17.3 kcal mol^{-1} at low temperatures, and 24.9 kcal mol^{-1} above about 40°; various preparative procedures do not alter this transition, and it is suggested that it is, in fact, intrinsic. Information on the anisotropy of conductivity in single crystals would be valuable.

b. Acid Salts

i. The KDP Ferroelectric Family (MH$_2$XO$_4$). The KDP family of materials is that based on potassium dihydrogen phosphate (KDP), with similar crystal structures,[13,69,73] which consist of an array of XO_4^{2-} groups (phosphates or, alternatively, arsenates) linked together by hydrogen (or deuterium) bonds into a three-dimensional network. The cations (M = K, Rb, Cs, NH$_4$) fit into interstices in the hydrogen bond network. The structural situation in the paraelectric phase[19,173] may be regarded as related to that in ice. We choose KDP as an example in discussing the crystal structure of compounds of this family. Every PO$_4$ tetrahedron is tetrahedrally surrounded by four more PO$_4$ groups, each linked by a hydrogen bond, with one proton in each hydrogen bond and two protons associated with each PO$_4$ group so that the anion may be formulated as $H_2PO_4^-$. The ferroelectric phase structure is ordered so that the hydrogen atoms are all covalently bound to the "tops" of the phosphate groups, in the posi-

tive direction of the orthorhombic c axis. On reversal of polarization, the protons move along the O—H···O bonds to become bonded to the "bottoms" of adjacent phosphates. The hydrogen bonds are almost perpendicular to the c axis, and the proton charge shift cannot account for the magnitude of the observed polarization, which appears to arise from accompanying small shifts in the heavy atom positions. In the disordered high-temperature phase there appears to be half a proton close to a particular phosphate group in each of its four bonds. Deuteron resonance experiments[61,174] yield a single resonance line, showing that the deuteron moves rapidly from end to end of the hydrogen bond above the transition temperature, but two resonance lines are observed in the ferroelectric phase. There is a dramatic isotope effect, deuteration of KDP increasing the ferroelectric transition temperature from 121 to 222 K; this isotope effect suggests a proton tunnelling process between the potential minima in the hydrogen bond and is confirmed by recent cold neutron scattering experiments.[175] "Ultraslow" hindered rotation of H$_2$PO$_4$ groups has been identified by proton spin–lattice relaxation measurements.[176] The proton dynamics have also been studied by ir.[177]

Rather recently, high-temperature phase transitions have been found in KDP and in its deuterated analog KD$_2$PO$_4$ near their melting points;[178] calorimetric, thermogravimetric, magnetic resonance and relaxation, ir spectroscopy, and X-ray and neutron inelastic scattering experiments were performed[179] and yielded the result that the transition corresponds to the onset of disordered, hindered rotation of the H$_2$PO$_4$ groups around all three axes. This conclusion was, however, contradicted by a subsequent report[180] on a similar high-temperature phase transition in RbH$_2$PO$_4$ at 86° (or 120°),[181] where the onset of a rotational transition of H$_2$PO$_4$ in RbH$_2$PO$_4$ is denied, as also for KH$_2$PO$_4$; instead a transition to a pyroelectric phase is claimed, where the protons attach to one upper and one lower corner of a PO$_4$ group. The latter interpretation, of a static structure for the high-temperature phase, is inconsistent with calculations of Adriaenssens and Bjorkstam[182] who suggest that an H$_2$PO$_4$ group reorientation process is also inadequate to explain the experimentally observed tenfold reduction in the nmr second moment over the temperature range concerned. They prefer to question, with Nicholson and Soest,[183] the reality of the phase transition, and ascribe the results to the known thermal decomposition which occurs just below the melting point of KH$_2$PO$_4$. This does not, however, accord with the phase transitions observed[180] in RbH$_2$PO$_4$ well away from its melting point, and also in KD$_2$PO$_4$.[178]

The high-temperature phase transition has been further investigated by measurement of the linear thermal expansion of single crystals,[477] by high-pressure differential thermal analysis,[478] and by hot-stage microscopy under polarized illumination, thermogravimetry, and differential scanning calorimetry;[479] there is now little doubt that the phase transition at about 180–200° exists, together with another at about 240°, very much closer to the melting point. A further transition proposed[477] near 100° seems, in fact, to arise either from evolution of trapped water[479] or from some decomposition.[480] The mechanism of thermal decomposition of the acid phosphates has been discussed in terms of mobile protons by Dombrovskii.[184]

Potassium Dihydrogen Phosphate. A number of systematic conductivity measurements on single crystals of KH$_2$PO$_4$ and also on KD$_2$PO$_4$ (90% deuterated) have been reported.[132,185-189,481] These experiments show

TABLE II. Conductivities of KH_2PO_4-Type Materials in Their Paraelectric Phases

Material	Ref	Direction[a]	Low temperatures			High temperatures		
			Temp[b]	$\sigma_0{}^c$	E^d	Temp[b]	$\sigma_0{}^c$	E^d
KH_2PO_4	132	Powder	$60 < t < 220$	3	13.2			
	300	$\parallel c$		0.05	12.5			
	300	$\perp c$		0.01	11.3			
	186	$\parallel c$	$-80 < t < 90$	0.79	13.4			
	187	$\parallel c$	$50 < t < 90$	0.26	13.9	$90 < t < 150$	350	19.1
	187	$\perp c$	$50 < t < 115$	0.58	14.1	$115 < t < 150$	800	19.6
	188	$\parallel c$	$-35 < t < 180$	0.13	12.7	$180 < t < 230$	100	18
	188	$\perp c$	$-35 < t < 180$	0.07	12.5	$180 < t < 230$	100	18
	481	$\parallel c$	$20 < t < 100$	0.02	12.2	$100 < t < 180$	1.8×10^4	22.8
$KH_2PO_4{}^e$	188			$\propto [SO_4{}^{2-}]$	11.9			
$KD_2PO_4{}^f$	189	$\perp c \approx \parallel c$	$-35 < t < 102$	0.03	12.2	$102 < t < 230$	250	19.0
KH_2AsO_4	199	sc	$0 < t < 110$	3	15.2	$110 < t < 180$	10^4	22.2
	202	sc (1592 Hz)			~ 10			
$KH_2AsO_4{}^e$	199	sc			13.0			
$NH_4H_2PO_4$	201	$\perp c \approx \parallel c$	$30 < t < 83$	1.54	14.4	$83 < t < 130$	6460	20.4
	202	$\parallel c$ (1592 Hz)	$40 < t < 150$	126	11.1			
	300				14.5			
	481	$\parallel c$	$20 < t < 140$	7.6	15.0			
	481	$\perp c$	$20 < t < 140$	17	15.7			
$NH_4H_2PO_4{}^g$	201	sc		<0.1	10–11			

[a] "sc" denotes single crystal, direction unspecified. [b] Temperature range, in °C. [c] Preexponential factor, in $ohm^{-1} cm^{-1}$. [d] Activation energy in $kcal\ mol^{-1}$. [e] Doped with $KHSO_4$. [f] KH_2PO_4 90% deuterated. [g] Doped with Ba^{2+} and with $SO_4{}^{2-}$.

that the conductivity is an activated process, for a plot of log σ vs. $1/T$ is linear in the low temperature paraelectric phase ($-80°$ to at least $90°$).[186,481] The conductivity is not markedly altered by deuteration[189] but increases proportionately to the concentration of sulfate "doped" into the crystal.[188] The conductivity parameters for KH_2PO_4 are presented in Table II. Some observers[186,187,481] find a knee in the log σ vs. $1/T$ curve at about $100°$, while there is also a change in the conductivity behavior near the phase transition at $180°$.[188,481] The $100°$ knee may be attributed to the loss of water, mentioned above,[477,479,480] for it is associated with a surface conductance which is irreversibly generated on heating.[481] The ionic nature of the conductivity can be deduced from observations of a polarization process on application of an electric field[186,187,481] and from electrolysis experiments, which yield hydrogen gas in a quantity corresponding to that expected according to Faraday's law;[185] protonic conductivity is inferred on account of the nature of the solid and the correspondence between the activation energies for conductivity and for slow deuteron interbond jumps.[186] These interbond jumps correspond to a low-frequency reorientation process observed by nmr, with a frequency from 10^3 to 10^5 Hz, while a high-frequency reorientation process, at 10^9 to 10^{12} Hz, which slows down on approach to the transition to the ferroelectric phase, is related to deuteron motion within the hydrogen bond. This conclusion is nicely supported by a recent dielectric investigation[190] of potassium hydrogen maleate, which crystallizes in such a way[191] that the intramolecular hydrogen bonds are all parallel along the crystallographic c axis. The low-frequency dielectric constant is largest along this direction and is associated with a dispersion having a relaxation time of 5.2×10^{-12} sec at $25°$ and an activation energy of $2.8\ kcal\ mol^{-1}$; this is most likely to correspond to the fast intrabond deuteron motion observed in the nmr relaxation experiments.[186]

The earlier experimental conductivity set-ups mentioned did not have guard rings, so that surface conductance is included in the reported conductivities. Surface conductance does not appear to be significant at low temperatures, however, since O'Keefe and Perrino[188] performed their measurements under pressures of water

vapor (to prevent decomposition of the KH_2PO_4) and found no significant effect of water vapor pressure on the conductivity below the transition at $180°$, while Harris and Vella[481] similarly find no effect below the knee which they observe at about $100°$.

O'Keefe and Perrino[188] have discussed the conductivity of KDP as an intrinsic property of the hydrogen bond network. They pointed to the fact that when the ordered ferroelectric phase transforms to the disordered paraelectric phase there will be certain high-energy[192] M defects, with a closer proton in one each of the upper and lower hydrogen bonds of the $H_2PO_4{}^-$ group. This defect may be considered to arise from a proton transposition from an upper bond (which then contains no protons and is called an L defect, by analogy with the Bjerrum[369] defect in ice) to a lower bond (which becomes doubly occupied, a D defect). Ionization of a pair of H_2PO_4 groups also occurs, perhaps by a proton transfer across a hydrogen bond

$$2H_2PO_4 \longrightarrow HPO_4' + H_3PO_4\cdot$$

where the superscripts indicate a negative and a positive charge, respectively, relative to the normal charge at that site.[22] The proton so created can then move through the crystal by a sequence of intra- and inter-bond transfers of protons, the latter across a PO_4 group. This would leave a chain of M defects, a high-energy state, in its wake and prevent the chain from further participation in the conduction process. Simultaneous migration of a D defect (or of an L defect, in the opposite direction) will avoid leaving a trail of M defects. L and D defects can be formed in processes independent from those forming ionic defects, and their concentrations will be independent.

The inter-bond proton transfer is not discussed in detail by O'Keefe and Perrino, but has been identified[176] with the slow H_2PO_4 rotation observed by nmr, because of the similarity of activation energies ($12.7\ kcal\ mol^{-1}$ by conductivity experiments, and $14.7\ kcal\ mol^{-1}$ in the nmr experiment, but largely influenced by the nature of the cation as indicated by data from isomorphic materials). The conductivities and their activation energies for KH_2PO_4 and KD_2PO_4 below $180°$ are rather similar, but

the KD_2PO_4 conductivity is a little smaller; this is not inconsistent with the rate-limiting step for the conductivity being that of an H_2PO_4 (or D_2PO_4) group rotation. It may be noted that this is opposite to the case in ice[370] where the limitation on the dc conductivity is ascribed to the minority ion states, and the dielectric relaxation to the motion of the majority orientational defects. The activation energy for tritium diffusion[193] in KH_2PO_4 at 0° is 3.8 kcal mol^{-1}, which is considerably different from that for conduction. This implies that, as for oxonium perchlorate and for ice, the major diffusion component is electrically inactive and overshadows the free-charge movement contribution to the diffusion.

The effect of sulfate dopant is believed to be the substitution of HSO_4^- for $H_2PO_4^-$, which involves the formation of an L defect. This defect may dissociate from the sulfate and contribute to or, in sufficient concentration, control the conductivity.

From the experimental data, a mobility of the L defect is calculated.[188]

$$\mu_L = 6 \times 10^{-10}\ cm^2\ V^{-1}\ sec^{-1}\ at\ 25°$$

The high-temperature activation energy, determined in crystals in which the phase change had apparently not occurred, is ascribed to the simultaneous thermal generation of ions and orientational defects and their simultaneous migration, from which an activation energy (5.4 kcal mol^{-1}) for ion formation and migration has been calculated. However, a later comment[189] attributes the high-temperature effects to the phase change, which renders the above analysis invalid. Harris and Vella[481] have noted the similarity in the activation energies for conduction in sulfate-doped KDP and in the lower temperature range for various samples of pure KDP (see Table II) and conclude that the conductivity in the lower temperature range is controlled by impurity-generated L defects and is not an intrinsic property of the hydrogen bond network as assumed by O'Keefe and Perrino.

Harris and Vella thus ascribe the activation energy in the lower temperature range, 12.2 kcal mol^{-1}, to the activation energy for L defect migration, while the activation energy in the higher temperature range, 22.8 kcal mol^{-1}, is larger by the amount required for thermal generation of L defects, viz., by 10.6 kcal mol^{-1}. The temperature of the knee in the log σ vs. $1/T$ curve will vary with crystal purity; in particular, the less defective crystals will have a knee at the lower temperatures. This conclusion is in conflict with that drawn from the suggestion[479] that the knee arises from release of trapped water, when its temperature will fall as defects increase.[477] O'Keefe and Perrino[188] may have suppressed the knee by their procedure of working within an atmosphere of water vapor, while Harris and Vella[481] may have enhanced the effect by continuously flushing their sample with dry nitrogen. This differing prediction as to the behavior of the knee temperature need not alter Harris and Vella's conclusion that L defects are the conducting species, for, if L defects are created during the trapping of water, loss of that water (but leaving the L defects behind) will require the thermal generation of further L defects, as observed.

It may be noted that the evidence for proton participation in the conduction is essentially circumstantial, since definitive electrochemical experiments (such as for KHF_2) have not been reported. It is, therefore, possible that the high-temperature conductivity (above 180°), at least, may be contributed to by the potassium ion as is the case for KHF_2 in its high-temperature phase (section IV.B.1.c). This possibility is worthy of careful investigation.

Bradley, et al.,[132] by means of ac conductivity measurements at 1592 Hz as a function of pressure up to 60 kbars and temperatures up to 220°, have established that the activation energy for conduction in powders decreases slightly with increasing pressure, whereas σ_0 is virtually constant. The pressure dependence of the conductivity yields an overall activation volume of -1.1 cm^3 mol^{-1}. Interpretation of this result is difficult. It is noteworthy that no knee in the log σ vs. $1/T$ curve is observed, perhaps due to impurity, or perhaps due to the use of compacted powders in sealed containers rather than the single crystals of other investigators.

Potassium dihydrogen arsenate (KDA), KH_2AsO_4, is isomorphous with KDP, and similar physical processes probably occur in the two materials. Epr,[194] nmr,[61,195,196] dielectric,[195,197] and cold neutron scattering[198] measurements confirm the existence of hydrogen motions, intra- and inter-bond.

The electrical conductivity of single crystals of pure and sulfate-doped KDA has been measured (along unspecified directions, probably parallel to the c axis) by Perrino, et al.,[199] using the same procedures as for KDP, viz., maintaining water-vapor pressures in the equilibrium range for KDA, and with unguarded gold electrodes. An activation energy for conduction of about 10 kcal mol^{-1} in KH_2AsO_4 is implied in a comment on unpublished work by Pollock and Sharan.[202] The conductivity data appear in Table II.

The pattern of the conductivity results conforms well with that for KDP, with a knee in the log σ vs. $1/T$ curve at 110°, corresponding perhaps to a possible phase change. Sulfate doping by 0.01 mol % increases the conductivity 100-fold and reduces the activation energy for conduction from 15.2 to 13.0 kcal mol^{-1}. The results are interpreted, by analogy, following the same mechanism as that attributed to KDP by O'Keefe and Perrino,[188] with the high-temperature activation energy being increased by the onset of ion formation, to which is attributed the difference in the activation energies, 7.0 kcal mol^{-1} (cf. 5.4 kcal mol^{-1} for the same process in KDP). This attribution will, of course, also be upset if the transition corresponds to an as yet undetected phase transition in KDA. From sulfate doping effects, a mobility of L defect migration is calculated

$$\mu_L = 2.4 \times 10^{-10}\ cm^2\ V^{-1}\ sec^{-1}\ at\ 25°$$

which is slightly lower than the corresponding (but perhaps spurious) value calculated for KDP.

Ammonium dihydrogen phosphate (ADP), $NH_4H_2PO_4$, is isomorphous with KDP, and similar physical processes probably occur in the two materials, although the phase transition at low temperatures is believed to be to an antiferroelectric phase.[19] Relevant nmr spectroscopic studies are mentioned by Blinc,[61] and a brief report has appeared on nmr in the isomorphous $ND_4D_2PO_4$.[200]

Electrolysis of ADP crystals yields hydrogen in the proportions expected from Faraday's law in accordance with a proton conduction mechanism;[164,201,202,436b] the possibility of other ion movements is conceded but this is believed to be unlikely. An earlier report[203] suggests, however, that ammonium ions may be the charge-carriers, on the basis of the loss in mass observed after current passage through a crystal. In the conductivity measurements reported below, no attempt was made to maintain the water-vapor or ammonia pressure within the phase stability region of the material; at temperatures above 40° there is evidence[481] to suggest decomposition by loss of ammonia, leaving a film of liquid phosphoric

acid on the crystal surface. This film increases the surface conductance and leads to a knee in the log σ vs. $1/T$ curve at temperatures above $80°$[201,481] which is, however, eliminated by use of a guard electrode. The conductivity is almost isotropic, some tenfold larger than in KDP, and there is little difference among the results from a number of investigators.[201,300,481] The conductivity data for ADP are listed in Table II.

The activation energy for conduction in Ba^{2+}- and in SO_4^{2-}-doped ADP[201] is about 10.6 kcal mol^{-1}, similar to the 12 kcal mol^{-1} observed in KDP, and this activation energy is also ascribed[481] to L defect motion. The activation energy for conduction in pure crystals is larger, about 15 kcal mol^{-1} (see Table II), so that, if L defects are also the charge carriers, the extra 4.4 kcal mol^{-1} must be that required for thermal generation of carriers. This amount is, however, very much less than the 10.6 kcal mol^{-1} required for the thermal generation of L defects in KDP. It is therefore suggested[481] that the difference arises from the presence of the hydrogen-bonded ammonium phosphate lattice in ADP. Incipient decomposition of the ADP may involve proton transfer from NH_4^+ to $H_2PO_4^-$ ions, to form NH_3 (an A defect) and H_3PO_4, as in the Herrington–Staveley[148] model for NH_4Cl. Motion (in unspecified ways) of the proton vacancies created by the A defects and of impurity-generated L defects is ascribed an activation energy of 10.6 kcal mol^{-1}, so that the excess 4.4 kcal mol^{-1} of activation energy may be ascribed to thermal generation of A defects. This is in contrast to earlier attributions[201,204] of the conduction mechanism to a proton motion solely within the $H_2PO_4^-$ hydrogen-bonded lattice. In view of these necessarily diffuse arguments in the analysis of the activation energies for conduction, it should not be forgotten that the 15 kcal mol^{-1} for the activation energy of conduction in pure ADP is very similar to the 14.7 kcal mol^{-1} ascribed to the activation energy for a rate-limiting H_2PO_4 rotation in KDP, as determined by nmr.[176]

Pollock and Sharan[202] have also examined the conductivity of single crystals of ADP, but without control of the water-vapor or ammonia pressures and with unguarded electrodes. Over the temperature range 40–150° they find ac (1592 Hz) conductivities about two orders of magnitude greater than the dc conductivities reported by others (Table II) and observe no breaks in the log σ vs. $1/T$ curve, which yields a single activation energy of 11.1 kcal mol^{-1}. Obviously, the two data sets cannot be easily reconciled. It has been suggested[1] that Pollock and Sharan were dealing with highly impure crystals; although there is no information on the quality of these commercially supplied crystals, this explanation seems less likely than that the high ac conductivity arises partly from an orientation polarization process, perhaps in a surface layer, which contributes only a transient in dc measurements. A large difference has similarly been observed between the ac and dc conductivities of lithium hydrazinium sulfate (see section IV.B.3.a.i). This hypothesis, however, requires testing before more can be made of it.

Harris and Vella[481] report that the conductivity of ADP is unaffected by voltage gradients as large as 10^9 V cm^{-1}, so that no electron injection into the ADP occurs.

Pollock and Sharan[202] also report on tritium diffusion measurements on ADP, which yield the following relation for the diffusion coefficient.

$$D/cm^2 \, sec^{-1} = 6.63 \times 10^{-5}e^{-9.3kcalmol^{-1}/RT}$$

The discrepancy between this activation energy of 9.3 kcal mol^{-1} for ADP and the 3.8 kcal mol^{-1} measured[193]

for KDP is noteworthy. Nevertheless, it is still much lower than the activation energy for conduction so that, again, there must be diffusion-active processes which do not involve electrical charge transfer, perhaps the diffusion of neutral ammonia molecules.[481] Because of the discrepancy between the ac and the dc conductivity data, the analysis of the relation between conductivity and diffusion coefficient, as presented by Pollock and Sharan,[202] should be reconsidered.[481]

ii. Alkali Metal Trihydrogen Selenites. The physical properties of the alkali metal trihydrogen selenites have recently been reviewed in connection with an investigation of their vibrational spectra.[205] $KH_3(SeO_3)_2$ contains sheets of selenite ions[206,207] and is not ferroelectric; the ferroelectric lithium[208] and sodium[207,209] salts contain three-dimensional networks of hydrogen bonds. Nmr relaxation measurements have been made on $MH_3(SeO_3)_2$ (M = Na, K, Cs—all ferroelectric, except for the potassium salt) in conjunction with measurements on materials of the KDP family.[176] The results are similar for the two families of compounds; as already noted for KDP, there is an "ultraslow" reorientation (correlation time for the Na selenite, $\tau_r = 10^{-3}$ to 10^{-5} sec) which, by analogy to KDP, is ascribed to SeO_3 group rotation. On the basis that the intrabond proton motion has a much shorter correlation time ($\tau_t = 10^{-12}$ sec) than the rotational correlation time, it is postulated that the expected dc proton conductivity of these compounds will be dominated by the slow reorientations of the SeO_3 groups.

The conductivities[210] of $NaH_3(SeO_3)_2$ and of its deuterated analog are similar at 25°, at about 10^{-9} ohm^{-1} cm^{-1}, with a small anisotropy and an activation energy of about 18 kcal mol^{-1}. There are indications from nmr relaxation times[210] of inter- and intra-bond proton motions. The activation energy for SeO_3 group rotation in this compound is 14 kcal mol^{-1}, so that there are contributions from other processes to the activation energy for conduction.

iii. Diammonium Orthoperiodate. Diammonium orthoperiodate, $(NH_4)_2H_3IO_6$, presents an interesting parallel with KDP. The IO_6 groups are linked into a three-dimensional network by hydrogen bonds,[211,212] in a fashion similar to that already described for KDP. An order–disorder transition associated with half of the protons in their hydrogen bonds occurs in the periodate at 254 K ($-19°$), in two steps less than 2° apart; it is suggested[212] that the first is the order–disorder process, while the second is a displacive transition following on from the first. Principal evidence for the order–disorder nature of the transition is a specific heat anomaly at this temperature and a decrease of the dielectric constant from about 180 just above the transition to 40 following a temperature drop of only 2°. The low-temperature phase may be antiferroelectric.[213]

The room-temperature conductivity is about 10^{-8} ohm^{-1} cm^{-1} and decreases with temperature in the same manner as does the dielectric constant.[214] This is the only comment which appears on the conductivity. No conductivity interference with dielectric constant measurement is reported, and the polarization is strictly proportional to the applied field up to the electric breakdown field of 40 kV cm^{-1}. This seems to suggest that proton conductivity in this compound is small or absent, and it is interesting to speculate why this might be so in spite of the structural similarity to KDP and ADP. The absence is difficult to understand in terms of the original hopping model described by Murphy[201,204] (see section IV.B.2.b.i) because the pattern of proton transfer should be the same for the two materials. If, however, a rotation

of the proton–oxygen complex, H_2PO_4 or H_3IO_6, respectively, is required, then the discrepancy becomes explicable, for the evidence for H_2PO_4 group rotation is clear while no such evidence exists for the more extensively hydrogen-bonded H_3IO_6 group.

$Ag_2H_3IO_6$ is isomorphous with $(NH_4)_2H_3IO_6$ and undergoes an order–disorder phase transition at about $-40°$. Similar considerations to those for the ammonium salt should also apply to this silver salt.

iv. Potassium Bisulfate. Potassium bisulfate, $KHSO_4$, has a structure[69,215] in which half of the sulfates form closed hydrogen-bonded dimers, while the other half form hydrogen-bonded chains. Rogers and Ubbelohde[216] have examined the conductivities of the melt and the solid frozen from it, and find an exceptionally low activation energy at temperatures well below the melting point of $207.1°$. The low-temperature dc conductivity is described by the equation

$$\sigma = 3.5 \times 10^{-7} e^{-1.8\,kcal\,mol^{-1}/RT} \; ohm^{-1}\,cm^{-1} \quad 23° < t < 93°$$

By contrast, just below the freezing point it is

$$\sigma = 6.8 e^{-15.3\,kcal\,mol^{-1}/RT} \; ohm^{-1}\,cm^{-1} \quad 93° < t < 168°$$

The current is ionic, for there are visible changes around the anode on passage of current. On the basis of these observations, then, together with the belief that the proton could enter both substitutional and interstitial positions, it was suggested that the proton was participating in the conduction process in the solid. Since the crystal structure of $KHSO_4$ was unknown at that time, the possibility of a proton transfer within the hydrogen bonded chain was not considered. The conductivities of the melts of $NaHSO_4$ and of NH_4HSO_4 were also examined, but apparently not those of the solids (both of which are ferroelectric, in contrast to $KHSO_4$). In view of these results, closer investigation of the conductivities of these salts is desirable.[482]

v. Alkali Metal Bicarbonates. An interesting group of materials from the present viewpoint is the alkali metal bicarbonates which form two different types of hydrogen-bonded structures: closed dimers for $KHCO_3$ and chain-bonded structures for NH_4HCO_3 and for $NaHCO_3$.[73] The dielectric properties[217,218] of compressed powders of these materials exhibit no effects attributable to the hydrogen-bonding structure (the hydrogen bonds are rather short, at 2.55 Å, for $NaHCO_3$). However, humidity appears to affect the dielectric properties by the formation of electrically conducting films of adsorbed water on the particle surfaces.

c. Acids

i. Oxalic Acid Dihydrate. Oxalic acid dihydrate, $(COOH)_2 \cdot 2H_2O$, has a structure[13,73,219] which contains spirals of hydrogen bonds in which the carboxyl groups are linked together through water molecules. Nmr measurements[220] and measurements of scattering of X-rays by vibrations in the crystal[221] show little evidence for molecular rotations.

The dc electrical conductivity[222] of compressed powders of oxalic acid dihydrate is largely time independent but non-ohmic from the lowest field strengths, and is much affected by the presence of water vapor. The conductivity is about 10^{-9} ohm^{-1} cm^{-1} at room temperature (at 20 kV cm^{-1}, calculated on an I/V basis), while an activation energy of 23.5 kcal mol^{-1} has been reported.[122] The conductivity of single crystals is largest in the direction of the spiral of hydrogen bonds.[222]

Electrolysis experiments in which the protons were intended to be absorbed by a palladium cathode and detected by dimension changes of the Pd lattice yielded variable and equivocal results,[222] while those using the Maričić gas collection cell[301] gave negative results.[131] However, when the applied field was sufficiently large to cause electrical breakdown, considerable proton discharge occurred (detected with the Pd cathode);[131] the crystal "healed" to its former resistance after the field was removed, even though black decomposition products could be seen. Recently, oxalic acid dihydrate has been electrolyzed in a gas collection system to yield hydrogen gas in the proportions expected for a proton conductor.[434] However, these experiments were apparently performed under high voltage gradients, and a similar effect of increased hydrogen yield at high voltage gradients applied to hemoglobin was noted. Therefore, this hydrogen production may be a field-induced effect. Dielectric results show a space-charge dispersion region and a 1 kHz absorption which decays with ageing, both ascribed to adsorbed water; no absorption due to crystalline water could be detected.[131] The dielectric absorption was small for single crystals, with no significant anisotropy.

Taken together, this evidence suggests that oxalic acid dihydrate is not a proton conductor, although the conductivity is enhanced by the hydrogen bonding. The non-ohmic behavior may arise from an injection process associated with the presence of the water of crystallization. The conductivities of compressed powders of a number of carboxylic acids, chain-bonded or with closed dimers, have been examined in relation to their hydrogen bonding by Pollock and Ubbelohde.[122,223] They find activation energies which are smaller the more extensive the hydrogen bonding, and interpret their results in terms of proton conduction. An objection to their results has been noted in section IV.B.1.a (benzoic acid).

ii. Amino Acids. The amino acids, $H_2NRCOOH$, form crystal structures which are significantly determined by the extensive hydrogen bonding which can occur. Thus, for different amino acids, structures occur consisting of chains, sheets, and three-dimensional networks of molecules linked by hydrogen bonds,[70,71] so that all amino acids do not fall correctly within the present class of hydrogen-bonded systems. Since their electrical properties are similar, however, they will be treated together.

The dc conductivity of amino acids has been extensively examined by Eley and colleagues, and most recently by Eley and Williams[224,225] who provide the most satisfactory data. The materials studied were valine, glycine, diketopiperazine, aspartic acid, glutamic acid, tryptophan, tyrosine, and leucine, each in the form of compressed powder disks, and, for the first three, also in the form of single crystals. In general terms, it was found that the dc conductivity is ohmic up to quite high field strengths, that the conductivity is perfectly steady over periods of time, that surface conductivity is not especially significant, and that σ_0 and the activation energy follow a single compensation law (see section IV.B.1.a) for the whole group of acids, which may be generally applicable to other crystals with the $CO \cdots HN$ scheme of hydrogen bonds. The experimental activation energies were found to be in the range from about 35 to 45 kcal mol^{-1}, which is rather higher than the activation energies found for inorganic proton conductors but still much lower than the 115 kcal mol^{-1} associated with the optical absorption edges which were also determined. The postulated explanation for this behavior is that electrons are injected (glycine is an *n*-type conductor)[224] from variable surface states, while the bulk conductivity is associated with the

hydrogen-bonded structure (as opposed to the predominantly surface character of the conductivity of acids such as benzoic acid). Eley and Williams[225] suggest that this mechanism would not apply to proteins, where the lower activation energies for conduction could imply an intrinsic generation of charge carriers.

Dry powders of amino acids do not display any large dielectric constant and have inappreciable dielectric absorption.[226-228] This suggests that the individual molecules are not free to rotate and that little ion transfer occurs, although it can occur under irradiation.[63] On adsorption of water, the dielectric constant rises rapidly, to level off near 2.5% water content.[227] No clear explanation of this behavior is offered.

Recent Raman studies[229] on L-alanine indicate that there is an effectively lowered symmetry of the crystal to the light scattering process, and this is taken to indicate a dynamic disorder of the proton in the hydrogen bond, even at low temperatures.

d. Hydrates

Hydrates, in general, have been rather arbitrarily placed in this category of hydrogen-bonded materials containing chains of hydrogen bonds broken by intermolecular links. This category is here extended to include materials such as borax, in which no directly linked chain can be perceived, but where rotation of a water molecule can create a new linkage and so provide such a chain. However, hydrates in which direct linkages exist, such as oxalic acid dihydrate, copper formate tetrahydrate, and lithium sulfate monohydrate, are treated in their more appropriate groupings.

The hydrates have a tendency to lose water under conditions of sufficiently low humidity or, perhaps, to adsorb water onto favorable surface positions at high humidities. Such more-or-less ephemeral layers of water may be expected to have a considerable influence on the electrical properties of these materials, if the water can participate in that process;[230] a particularly clear example of this apparently reversible behavior occurs with sodium thiosulfate pentahydrate.[231] Thus, on studying the reports below, the reader will begin to see a pattern emerging of properties which appear to be highly dependent on surface conditions; a similar conclusion holds for ice. Surface area is particularly large in powdered materials, and any such behavior will thus be prominent in powdered materials. Control of these conditions does not appear to have been fully mastered by experimentalists in general, and there are, therefore, considerable discrepancies between experimentally determined quantities as a result, which must be borne in mind in assessing the data reported here.

Although the surface properties of materials such as oxides are significantly affected by water vapor (cf. section IV.A.1.a), it is not certain to what extent the problem of surface conditions pertains to other nonhydrated materials. Certainly, however, the higher the resistivity of a material, the more likely it is that surface contamination will significantly affect the observations[127] and often without the experimentalist being adequately aware of the problem.

i. Cupric Sulfate Pentahydrate. Cupric sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, has four of its water molecules coordinating the Cu^{2+} ion, with the octahedral coordination shell completed by oxygens from sulfate ions.[232] The fifth water molecule acts as a bridge between the coordinated water molecules of neighboring cations, thus perhaps providing a convenient path for proton transfer.[233]

Nmr of deuterated material[234] indicates fast molecular reorientation about the bisecting axis of each water molecule above room temperature, but this reorientation is quenched at lower temperatures. Free rotation of the water molecule does not occur up to the dehydration point. The dc conductivity is reversible with temperature changes[235] up to 80°. A discussion of the dielectric properties appears in a report by Barrer.[236] Williams, Sykes, and Schneider[233] have reported on proton injection experiments with single crystals of cupric sulfate pentahydrate using electrodes consisting of saturated aqueous solutions of copper sulfate, with the positive electrode acidified with sulfuric acid to pH 0.1–3.0. The currents observed are linear with applied field to about 10 kV cm^{-1}, but are superlinear thereafter with a steep rise at a distinct voltage. The conductivity parameters are evaluated on space-charge theory; the transition depicted appears to be that from ohmic to approximately square-law dependence (see section II.C.3) but is treated as a trap-filled limit to yield a trap density of 10^{13} cm^{-3}. A carrier mobility is (correctly) calculated from the square-law region as 1×10^{-5} cm^2 V^{-1} sec^{-1}.

To demonstrate that injection of protons occurred, the aqueous anode solution was replaced with a tritiated one and the radioactivity in the crystal measured after 30 hr, both with voltage applied and without; the 2.5-fold increase in the activity when the sample was subjected to a field indicated tritium injection. By contrast, experiments with silver paste electrodes on the crystal yielded currents two to three orders of magnitude lower than with liquid electrodes. While it is probable that proton injection did indeed occur in these experiments, this may have been along cracks and dislocations in the crystals aided by water diffusion down these dislocations, as has been found to be the case with sucrose.[488] More definitive evidence with solid proton-injecting electrodes is required before proton injection and conduction can be accepted.

The diffusion of tritium through cupric sulfate pentahydrate has been measured,[193] and an activation energy of 5.3 kcal mol^{-1} is reported.

ii. Borax and Tincalconite. Borax, $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$, has a somewhat complex structure[237] as may be anticipated from the chemical structural formula. In essence, $[B_4O_5(OH)_4]$ anions are linked through pairs of hydrogen bonds into chains along the c axis of the structure, and such chains alternate with lines of Na$^+$ ions along both the a and b axial directions. The Na$^+$ ions are surrounded octahedrally by water molecules. Each hydroxyl group of an anion is hydrogen-bonded to a water molecule, and these molecules are so arranged that a proton transfer line can be visualized in the b direction (but in no other); this line is not a continuous hydrogen-bonded chain, but it is suggested[238,239] that the water molecules are sufficiently close (3.0 Å) for a hydrogen bond to form when a proton is rotated onto the oxygen-oxygen line. Borax dehydrates spontaneously below 14 mm (60% relative humidity) at 25°, to an amorphous phase.[240] A pentahydrate, $Na_2B_4O_7 \cdot 5H_2O$, tincalconite, forms by crystallization from hot aqueous borax solutions.

Nmr analyses of borax[241-243] are generally in rather poor agreement, partly because of poorly characterized mixed borax and tincalconite (or other hydrate) samples, partly because of saturation of signals, and partly because of the complexity of the data. It seems clear, however, that there are two major components to the signal: a broad line (width, 14 G) and a narrow one (7 G). The broad signal is attributed to rigid and flipping water molecules, while the narrow signal is due to one of the water molecules rotating about its bisectrix, or about a hydro-

gen bond; the latter signal may also be contributed to by the lower hydrate phase.[243] The complicated crystal structure, with 20 protons in the formula unit, makes analysis of the experimental data exceedingly difficult, however, and further interpretation is necessary especially in respect of temperature effects.

Dielectric experiments[244-246,248,249] on compressed powder pellets yield a stable spectrum at high humidities[244] (>60%) with two major components, a low-frequency component probably due to space-charge polarization because it is considerably increased by the use of blocking electrodes (aluminum electrodes attached with petroleum jelly) and a higher frequency dispersion with an activation energy of 14.3 kcal mol^{-1}. This dispersion moves to lower frequencies on ageing the pellet, especially at low humidities, and seems to be associated with adsorbed moisture which partly moves to sites of stronger adsorption, and is partly desorbed. This absorption is much less marked with single crystals,[244-246] which also display a thickness dependent low-frequency space-charge polarization, together with other possible low-frequency absorptions whose origin is not clear.

Electrolysis experiments have been performed on powder pellets[239,244,247] and yield hydrogen gas in amounts from 5 to 50% of that expected according to Faraday's law assuming proton conduction. The conductivity of these pellets is constant up to about 1.5 kV cm^{-1} (depending on temperature), but rises thereafter. The ac conductivity (50 Hz) of the powder is about 8 × 10^{-8} ohm^{-1} cm^{-1} at 30°, and about 3 × 10^{-8} ohm^{-1} cm^{-1} at 30° for 90% deuterated borax. This conductivity decreases by an order of magnitude on the loss of one-third of the mass of the sample by dehydration.[238] The single crystal dc conductivity is highly anisotropic,[239] being three orders of magnitude larger along the b axis (10^{-9} ohm^{-1} cm^{-1} at 25°) than along the directions normal thereto. All the conduction curves show more or less definite breaks at about 20-30°, with stable activation energies above the break (15 kcal mol^{-1} parallel to the b axis, 11.5 kcal mol^{-1} along the c axis, and 16.7 kcal mol^{-1} along the perpendicular to the b and c axes), and lower values below the break.

While Maričić and colleagues (upon whose work most of the above data are based) observed stable currents or even currents which rose as a function of time, with powder pellets and with similar pellets with a graphite admixture at the electrodes, van Beek[248] and also Giesekke and Glasser[244] observed falling currents, as would normally be expected as a result of space-charge polarization (cf. also the discussion on Li$_2$SO$_4$·H$_2$O). This is very puzzling and leads to some contradictions in conclusions, but can be reconciled if Maričić, et al., worked under conditions of high relative humidity, when adsorbed water would be present on the powder surfaces (especially fine-grained powder was used by them) and act as a proton source, while the others worked under lower humidity conditions (van Beek[248] reports resting his samples at 50% relative humidity; Giesekke and Glasser[244] worked in a laboratory at high altitudes with generally low humidity, as they report). This will tend to confirm the suggestion that the proton conductivity through the crystal is low (but not absent), while most of the proton conductivity is along adsorbed water layers at crystallite surfaces.[244] There seem to be parallel proton and electron conduction paths in borax. It would appear that Maričić, et al.'s, low frequency conductivities for powders (with an activation energy of about 26 kcal mol^{-1}) may refer to an adsorbed water phase; under the conditions of his experiments van Beek[248] could obtain

no reliable values of the dc conductivity. van Beek has also examined the dc space-charge limited currents which he finds to be more reproducible,[248] and finds that they are, as expected, proportional to the square of the voltage. From this proportionality he calculates a mobility for the injected charge

$$\mu = 1.7 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$$

which appears to be unacceptably high for protons. Correspondingly, he finds a low concentration of charge carriers (1 in 10^{11}).

The nmr and conductivity evidence for some form of transition below about 20° are rather ambiguous. At least part of these observations may arise from "freezing" of adsorbed water below this temperature. There is no evidence for an actual phase transformation, and the effect (if real) may simply reflect the slowing-down of the reorientation process of the water molecule. If, however, it is due to this, it is difficult to see why it should be observed in all three single-crystal directions[239] unless all three conduction paths—one protonic, the other two supposedly not—involve the same reorientation as the rate-limiting step for conduction.

Tincalconite, Na$_2$[B$_4$O$_5$(OH)$_4$]·3H$_2$O, is believed from nmr evidence to contain the borate ion as does borax,[242,250,251] but the structure is as yet incompletely determined.[252] Tincalconite crystallizes from aqueous borax solutions at temperatures above 70°. The nmr spectrum[243] contains a narrow line, indicating that all the water molecules are rotating, and begin to "freeze-in" only below 150 K. Electrolysis experiments[131] on tincalconite powder pellets yield hydrogen gas with proton efficiencies (at 61°) of 5% at fields of 1 kV cm^{-1}, rising to 35% at fields of 6.5 kV cm^{-1}; gas evolution was also observed at 26°. During these experiments the relative humidity was low, 35%, and the current fell as electrolysis proceeded according to an equation of Rosenberg's which implies depletion of the proton source.[253] The dielectric data obtained are rather similar to those for borax, arising from adsorbed water. The dc conductivity of powders has a notably low activation energy of 2.1 kcal mol^{-1} below 50°, with a break near the borax–tincalconite transition temperature. Many of the electrical properties of tincalconite are dependent on the presence of adsorbed water, but it seems that there is sufficient evidence to justify further interest in the material as a potential proton conductor.

iii. Partially Oxidized Platinum Chain Compounds. A new class of materials has recently been characterized,[254] consisting of square-planar metal complexes which, in the solid state, have the squares stacked one above the other with direct interaction between the metal ions in a direction perpendicular to the plane of the complex; a similar set of materials contains alternate square-planar and octahedral complexes in which the metal ions are halogen bridged. Such materials have been shown to have a highly anisotropic electrical conductivity, better by some 100-fold in the direction of the metal chain, and a "metallic" type of conductivity has been postulated in the chain direction,[255] perhaps due to correlated electron hopping.[256] There is no reason to suspect the presence of any charge-carriers other than electrons for the group of these materials which contain a regular arrangement of metal ions,[257] e.g., M(II)···M(II)···M(II)···, or ···M(II)···Cl···M(IV)···, etc., but there is strong evidence for ion carriers in some partially oxidized examples of these materials, especially at higher voltage gradients.

Conductivity measurements of interest in this respect have been reported on two groups of partially oxidized platinum chain compounds; the one group accommodates the partial oxidation of the Pt(II) (to Pt(IV), formally) by the presence of halide ions to preserve the charge neutrality,[258,259] e.g., $K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$, while the charge neutrality is maintained in the second group by a decrease in the proportion of the noncomplexing cation,[260,261] e.g., $K_{1.74}Pt(CN)_4 \cdot 1.8H_2O$. These materials change toward the fully reduced state when an electrical field is applied, but accommodate this change rather differently in the two cases, apparently losing bromine from the halogenated compounds, and accepting charge-compensating protons in the group in which the complement of cations is deficient. The experimental observations on single crystals of these compounds at sufficiently high field strengths are that chemical reactions commence at the anode and/or cathode and proceed through the crystal toward the opposite electrode.

The anode reaction on the cation-deficient compounds yields an acidic product, suggesting incorporation of protons to form, for example, $K_{1.74}H_{0.26}Pt(CN)_4 \cdot xH_2O$. The protons may come from the surface or from decomposition of the water of crystallization, with the latter being less likely because "drier" electrodes are observed to be more rapidly depleted of protons by the electrochemical action.[260] At high field strengths, a reaction also occurs at the cathode[261] which appears, in this case, to result from decomposition of the water of crystallization and ejection of K^+. Some of these reaction products appear to be proton conductors, and a solid-state protochemical cell has been set up[261] which yields an open-circuit potential of about 0.5 V. The conduction process in the halogen-containing compounds also leads to an oxidation–reduction process, but in this case the halogen ions apparently become discharged to form the halogen gas, and the electrons so released reduce the platinum fully to Pt(II). The details of the conduction processes have not been fully elucidated yet.

It is interesting to note in this connection that Errera and coworkers[262] have found unusual dielectric properties in some platinum cyanide complex compounds such as $MgPt(CN)_4 \cdot 7H_2O$, $Y_2Pt_3(CN)_{12} \cdot 21H_2O$, and $BaPt(CN)_4 \cdot 4H_2O$, which have been ascribed to dipole orientation of the water molecules. Such orientation is not usually observed in hydrates.
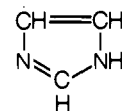
iv. Miscellaneous Hydrates. In general, hydrates may be expected to exhibit dielectric absorption at low frequencies, if they absorb at all,[64,263,264] and this absorption, together with the dc conductivity, will tend to be ascribed to proton motion although more positive evidence for this is difficult to find. The influence of water on the physical properties of crystalline hydrates was discussed in a conference in 1953, and reviewed there by Wooster,[265a] while Smyth,[42] Meakins,[64] and Hasted[266,360b] review the dielectric behavior of hydrates, the last most recently. In general, the dielectric loss due to the water in hydrates is small. On the other hand, nmr gives clear evidence of water molecule rotation.[267] The principal reason for the difference is that rotation of water about its twofold axis involves no dipole reorientation and so will be invisible in the dielectric spectrum.

Some hydrates for which mobility of the water has been invoked to explain their dielectric behavior (in addition to those discussed more fully in other sections) are: $Na_2HPO_4 \cdot 12H_2O$, $Na_2SO_4 \cdot 10H_2O$, $Na_2CO_3 \cdot 10H_2O$;[246] $MgPt(CN)_4 \cdot 7H_2O$, $Y_2Pt_3(CN)_{12} \cdot 21H_2O$, the corresponding calcium and strontium compounds, and also $BaPt(CN)_4 \cdot 4H_2O$;[262] $NH_4Cr(SO_4)_2 \cdot 12H_2O$;[268] pinacol

hydrate, $(CH_3)_2C(OH)C(OH)(CH_3)_2 \cdot 6H_2O$;[269] $Na_2S_2O_3 \cdot 5H_2O$;[231] $CaSO_4 \cdot 2H_2O$, $MgSO_4 \cdot 4H_2O$.[236] It is not suggested that this list is complete.

e. Hydrogen-Bonded Molecular Species

i. Imidazole has a monoclinic crystal structure in which the planar imidazole molecules are linked in a hydrogen-

bonded chain along the c direction, with the hydrogens in ordered positions in the bond.[270] The N—H···N distance is 2.81 Å at room temperature, which is short for a bond of this type. Riehl[271] first pointed out the intrinsic interest of this system and the possibilities of proton conduction therein.

A number of reports on the spectroscopic properties of imidazole have appeared.[272] Zimmermann studied the ir and Raman spectra of imidazole powders and suggested that these spectra could be explained by assuming a proton tunnelling in a nearly symmetric double well potential.[60,273] More recent work (ir,[274] Raman,[275] nmr,[276] and esr[277]) has, however, tended to dispute this interpretation and to suggest that the broadened spectra can be explained by other means, such as coupling between N–H and N,N stretching vibrations, without tunnelling.[278] First measurements of the conductivity of imidazole powders[279] showed the necessity of very careful purifications; zone-refinement is generally the method of choice. Pigoń and Chojnacki[280] determined the anisotropy of the surface conduction and showed that this conductivity is a maximum in the c axial direction, but approximately isotropic in the ab plane. These early workers assumed that conduction was electronic[281] and did not examine it for a protonic component.

More recently, the protonic conduction has been studied independently by Kawada, McGhie, and Labes[282] on powders and single crystals, and by Chan-Henry and Glasser[283] on powders. Electrolysis of both powders and single crystals in the c direction yielded hydrogen in almost the proportions expected according to Faraday's law (ca. 90% of that expected from a protonic current). In the a direction, which has a c component, electrolysis also yielded hydrogen gas but in much smaller proportions, only about 30% of that expected according to Faraday's law. Surface conduction could not be excluded from any of these experiments.

The conductivity at 1 kHz of molten imidazole,[282] which is also extensively associated, is governed by the expression

$$\sigma = \sigma_0 e^{-5.3 \text{kcal mol}^{-1}/RT}$$

From Zimmermann's estimate[273] of the equilibrium constant for self-ionization of the imidazole, this yields an estimate of a proton mobility of greater than 4×10^{-3} cm^2 V^{-1} sec^{-1}, a value comparable to that found in liquid water. In the frozen, polycrystalline, solid phase, the ac conductivity had an activation energy of 82 kcal mol^{-1} at high temperatures and 23 kcal mol^{-1} below 75°.

For single crystals, the dc conductivity was measured with a guard-ring system and found to be 10^3-fold greater in the c direction than in the a direction, consistent with the fact that the hydrogen bonding is also directed along the c direction. The c conductivity is about 10^{-13} ohm^{-1} cm^{-1} at room temperature. The activation energies are

39 kcal mol^{-1} in the c direction, 44 kcal mol^{-1} in the a direction at high temperatures (above about 60°), and 25 kcal mol^{-1} at lower temperatures (these values of the activation energies should be regarded as upper limits because they were determined by continuous cooling rather than by equilibrium measurements). It will be noted that the conductivities are rather lower than generally found for inorganic proton conductors, such as KH$_2$PO$_4$, while the high-temperature activation energies are nearly double. No polarization effects are reported for the single-crystal measurements, although they appear in a figure dealing with the electrolysis measurements.[282] This indicates a current which decayed over 0.5 hr; the decay being larger for less pure samples indicates that at least part of the polarization was due to the presence of impurity ion charge-carriers. Dielectric measurements showed an absorption,[284] which did not disappear on drying, having two components: one was a broadened Debye dispersion with relaxation time 2 × 10^{-5} sec at 65°, and with an activation energy of 26 kcal mol^{-1}; the second was a low-frequency dispersion perhaps arising from space-charge polarization.

A proton conduction mechanism was postulated involving cooperative proton transfer of a positive ion state along the hydrogen-bonded chain of molecules and discharge at the cathode, followed by a rotation of the molecules in order to reorient the chain into its original direction.[282] The reorientation is believed to be the rate-limiting step in the conduction and is conceived to be associated with the transfer of an L defect back down the chain, D defects being thermally too expensive in these short hydrogen bonds. Daycock, et al.'s, value for the rotational energy, obtained by nmr[285] (3.7 kcal mol^{-1}), is regarded as too small for a nonplastic crystal like that of imidazole, and the total activation energy of 39 kcal mol^{-1} is ascribed to the rotational orientation. This cannot be correct, however, for the activation energy must be made up of contributions from the various steps involved in the conduction, i.e.

$$E = \tfrac{1}{2}E_D + E_M + E_R$$

where E_D is energy of dissociation, E_M the energy of proton transfer, and E_R the energy of the reorientation. The orientation energy may rather be equated with the activation energy for the dielectric relaxation measured on imidazole powder (26 kcal mol^{-1}). Then, assuming that E_M is negligible for a hydrogen-bonded system, this yields a value of 38 kcal mol^{-1} for the dissociation energy. This is much larger than the value (about 10 kcal mol^{-1}) found by Kawada, et al.,[282] for dissociation in molten imidazole.

The reorientation process has been the source of some discussion. Rotation of the imidazole molecules within their own plane would leave them incorrectly oriented, while rotation about an axis within their own plane would require large energies in the close-packed structure. Thus, a "tour" mechanism has been suggested, with the proton passing around the ring via the intervening carbon atom. This could occur either by the formation of a methylene group at the carbon atom[277,286] or by a cooperative transfer of the protons around the ring.[284] Such mechanisms are supported by the known lability of the proton attached to the carbon. If such a mechanism is correct, the analysis above of the activation energies for conduction and dielectric relaxation cannot be maintained, and a more detailed analysis must be made of the source of the dielectric relaxation.

Self-diffusion measurements on imidazole labeled with

^{14}C or with tritium have also been performed[287] (with respect to the tritium labeling, it should be noted that this was done in aqueous solution so that the hydrogen bound to both the nitrogen and to the unique carbon would have exchanged;[277,288] in view of the results obtained this is, however, unimportant). The self-diffusion coefficients in the a direction for both the ^{14}C and the ^{3}H diffusion were found to fall on the same temperature curve, following roughly the relation

$$D/\text{cm}^2\,\text{sec}^{-1} = 10^{25}e^{-60\text{kcal mol}^{-1}/RT}$$

These results are in qualitative agreement with others for nonplastic molecular crystals. The rate of recombination of imidazole free radicals produced by irradiation has also been followed by epr;[287] this rate is expected to correlate with the diffusion rate. Indeed, an activation energy of 55 kcal mol^{-1} was determined, but the diffusion coefficients so determined were two orders of magnitude higher than those determined in the self-diffusion experiments. Several reasons are adduced for this, based on the different conditions in the two experiments. It is concluded that diffusion proceeds via a molecular mechanism, and that there is no evidence for a contribution from a cooperative proton transfer process.

The rather similar solid-state properties of imidazole and 1,2,4-triazole have been noted.[277] The conductivity of benztriazole (and of related compounds) has recently been measured,[483] and the activation energy was found to drop from 21.8 kcal mol^{-1} under vacuum to 17.3 kcal mol^{-1} in ammonia. The relation of the results to possible proton transfer is briefly discussed.

ii. Urea (and Related Compounds). Urea, (NH$_2$)$_2$CO, has a crystal structure[70,289] with chains of molecules lying in alternate, antiparallel lines along the unique c direction of the tetragonal structure. The molecules are linked within their chains and between chains by hydrogen bonds. Spectroscopic evidence of various kinds suggests that the molecule librates moderately freely about its twofold axis,[290] with an activation energy for reorientation about the C=O bond[290a] of 12 kcal mol^{-1}.

The dielectric properties[284] of urea powders after drying are qualitatively similar to those of imidazole powders, but the dispersion is four times broader and the relaxation time is 10^3 times longer (3 × 10^{-3} sec at 70°), while the activation energy is similar at 23 kcal mol^{-1}. There is little polarization on application of a dc potential, and the conductivity is ohmic to about 5 kV cm^{-1}, showing signs of saturation at higher fields; the conductivity was 8.3 × 10^{-10} ohm^{-1} cm^{-1} at 60° when the pellet was subjected to a hard vacuum for 15 min before pressing. The activation energy for conduction[483] is 10 kcal mol^{-1}. Electrolysis yields no gas.

Injection experiments using a Pd|H anode failed. A "sandwich" pellet with imidazole on the anodic side was made up;[283,284] when potential was applied the current rose slowly to a value 100 times that for the equivalent urea pellet, and hydrogen was evolved at 90% efficiency according to Faraday's law, assuming proton conduction. Similar experiments with single crystals of urea and imidazole anodic pellets yielded a fourfold increase in conductivity in the a direction, but a 100-fold increase for the c direction. Hydrogen gas was collected from the c-axis experiment at 100% efficiency. The "sandwich" sample obeyed Ohm's law when the applied voltage was varied.

Injection experiments with deuterated imidazole[283,284] yielded hydrogen gas with only 2% of deuterium. This seems a clear proof of a cooperative (Grotthus) proton transfer process in urea, as deuterium gas should have

been produced had the injected deuterons been transferred by an interstitial mechanism (cf. discussion below).

According to the above results, urea is largely incapable of generating its own charge-carriers, but injection of a proton probably forms a charged D defect which can then migrate through the urea. There is difficultly, however, in understanding why this process should operate best in the c direction when the urea libration would indicate a more favorable rotational contribution normal to that direction.

Similar injecting effects from imidazole have been observed[283] in thiourea (which is ferroelectric and is believed to be an electronic conductor[291,483] under noninjecting conditions), benzimidazole, and succinimide. The gas evolved from a succinimide pellet using deuterated imidazole on the anodic side contains both H_2 and HD (but no D_2). This is interpreted as indicating both cooperative proton transfers and interstitial proton migration in succinimide.

Proton conductivity has been attributed to acetamide[292] ($\sigma = 5.6 \times 10^{-8}$ ohm^{-1} cm^{-1} at 82° for 1 kHz; activation energy, 34 kcal mol^{-1}) and the mechanism discussed, but the phase[13] (trigonal, or metastable orthorhombic prepared from the melt) is not clear; further details are not available. A high solid-state conductivity has been observed[293] in N,N-dimethyl- and N,N-diphenylacetamide.

iii. Purines and Pyrimidines. Some work has been done on the electrical properties of purines and pyrimidines, which are components of nucleic acid, principally treating them as electronic conductors.[294,494] An investigation by Thomas and coworkers[127,295] deals with the possible protonic conductivity of isocytosine.

Isocytosine, 2-amino 4-oxopyrimidine, crystallizes with two tautomers linked by hydrogen bonds[296] in a manner akin to the pairing of bases in DNA. Proton transfers would invert the tautomers, and sustained currents requires rotation of the molecules to reverse the molecular chain into its original orientation. Preliminary investigation[295] indicated phenomenal proton injection currents into isocytosine single crystals from Pd|H anodes, with or without a guard-ring system to remove surface currents. Later experiments, however, indicate numerous complicating features.[127] Thus, there is enhancement of the conductivity by the presence of various vapors (especially that of water), and nonohmic, injection behavior is observed for various electrode types irrespective of bias direction. These results are taken to suggest field dissociation of the adsorbed vapor, rather than charge injection, for samples exposed to water vapor. Carefully dried crystals have very low bulk conductivity, but the conductivity of carefully dried powders is three orders of magnitude larger, showing the importance of the surface conductivity. It must be concluded that isocytosine is not an intrinsic proton conductor.

Nmr work, in connection with these studies, on cytosine and cytosine monohydrate crystals,[297] in both of which the cytosine molecules are hydrogen-bonded in ribbons,[484] provides no evidence for rotation of the cytosine molecules, though the water molecule in the hydrate may rotate with an activation energy of about 4.3 kcal mol^{-1}.

3. Materials with Linked Chains of Hydrogen Bonds

While materials in the previous class of hydrogen-bonded molecular systems may be able to sustain a cooperative proton transfer, the chain reorientation required

for conduction may be conceived to be difficult. For the materials in the present group, where the hydrogen bonds are directly linked, there may be much less difficulty, and it is among this group of materials that evidence of fast ion transport should preferentially be sought; indeed, it was for ice (see below) that results indicating high proton mobilities were first obtained. Present evidence, however, is unclear on this point and it remains to be proven that semiconductor-like energy bands can be usefully attributed to a proton conductor.

The materials to be discussed fall naturally into three categories: (a) one-dimensional linked chains of hydrogen bonds (as in $Li_2SO_4 \cdot H_2O$), (b) sheets of hydrogen bonds (as in $Cu(HCOO)_2 \cdot 4H_2O$), and (c) a three-dimensional network of hydrogen bonds (ice). All of the materials considered in this category display signs of some freedom of motion for the proton in the hydrogen bond, such as disordering of the protons in ice and in copper formate tetrahydrate, or large librations of the water molecule in lithium sulfate monohydrate; there are also indications of proton conductivity in a number of the materials. A close connection between these two properties, of molecular or proton mobility and conductivity, is clear, for in corresponding materials in which there is little sign of proton mobility within the hydrogen bonds (such as oxalic acid dihydrate) there is also little indication of proton conduction, while in order–disorder ferroelectrics (such as KH_2PO_4) there is clear evidence of proton conduction.

a. Chains of Hydrogen Bonds

i. Ionic Materials. Lithium sulfate monohydrate, $Li_2SO_4 \cdot H_2O$, crystallizes in a monoclinic noncentrosymmetric space group,[298] is pyroelectric,[299] and may be piezoelectric.[300] The structure consists of Li^+ and $SO_4{}^{2-}$ ions, to the latter of which the water molecule is strongly hydrogen bonded. The water molecules are themselves linked by hydrogen bonds in a zig-zag chain along the b axis, to yield a potential path for cooperative proton conduction. Nmr[301-303] and structural data are consistent with a large-amplitude hindered rotation of the water molecule about its bisector, with an amplitude of oscillation of 20–30°. The nmr spectrum[301] contains two components, a broad line and a narrow one. This narrow component corresponds to an appreciable proportion of the water present, and it is not believed to be due to adsorbed water. However, special endeavours were made to obtain fine-grained powder by rapid precipitation from solution, and the possibility of the narrow component arising from relatively free water of crystallization near surfaces cannot be ignored. Hirahara and Murakami[303] ascribed a narrow line in their single-crystal experiments to water contained in cracks.

Electrolysis[301] of compressed pellets of $Li_2SO_4 \cdot H_2O$, with graphite admixture at the electrodes, yielded currents which increased with time to a more-or-less stable value, together with the evolution of hydrogen in proportions from 30 to 100% of that expected for proton conduction; this is taken as evidence for at least a partial proton conduction. The rise in current with time is contradicted by van Beek,[304] who observed the more typical polarization behavior of a falling current. As with borax, it is probable that the discrepancy arises from different working humidities or conditions on the powder surfaces, and Giesekke[131] has confirmed decay of the dielectric absorption at low humidities. Moreover, Thomas and Clarke[305] report a 10^6-fold decrease in surface conductivity on purging a conductivity cell containg single crys-

tals of $Li_2SO_4 \cdot H_2O$ with ultradry nitrogen, and find that their resultant conductivities are some eight decades lower than those of Maričić, et al., but compare well with those of Gurevich and Zheludev.[306]

Thomas and Clarke[305] have made a thorough study of the dc conductivity of single crystals of $Li_2SO_4 \cdot H_2O$ using platinum electrodes and a Pd|H proton-injecting electrode. They report an ohmic b-axis conductivity using platinum electrodes, up to 10 kV cm^{-1}, which follows the law

$$\sigma/\text{ohm}^{-1}\,\text{cm}^{-1} = 5.0e^{-20\text{kcal mol}^{-1}/RT}$$

No mention is made of time-dependent effects. With the Pd|H electrode, on the other hand, non-ohmic behavior appears, particularly along the b direction. This non-ohmic current is, following space-charge theory, proportional to V^2/d^3 (where V is the applied voltage, d the sample thickness). Measurements with and without a guard ring show that both the surface and volume currents are non-ohmic, while the surface conduction (even after purging of the cell) is more than half of the total conductivity. The conductivity in the ohmic region under injecting conditions yields (for the b direction, presumably) the following law.

$$\sigma'/\text{ohm}^{-1}\,\text{cm}^{-1} = 0.4e^{-18.3\text{kcal mol}^{-1}/RT}$$

The smaller value for the preexponential factor under injecting conditions ($\sigma_0 = 0.4$ ohm^{-1} cm^{-1}) as compared to the value under noninjecting conditions ($\sigma_0 = 5.0$ ohm^{-1} cm^{-1}) is unexplained.

Dielectric studies by van Beek[304,307] reveal that there is a low-frequency space-charge dispersion below 0.1 Hz, but only in single crystals cut perpendicular to the b axis; the space-charge origin of the dispersion is confirmed by comparison with the rate of decay of the dc conductivity. The protonic contribution to the conductivity is found to be about 10^{-10} ohm^{-1} cm^{-1} (which is much greater than the corresponding value, 3 × 10^{-14} ohm^{-1} cm^{-1}, reported by Thomas and Clarke[305]). The highest frequency dielectric dispersion (around 1 kHz) is ascribed to motions associated with the water of crystallization.

Thomas and Clarke's results[305] seem to be the most reliable yet available because of the low conductivity which they found, suggesting reduced surface conduction. Even in their case, surface conduction was not absent. Their results tend to confirm proton conduction through the observation of space-charge injection which is direction-dependent, being much the most prominent in the b direction. From space-charge theory, they obtain an effective mobility for protons of about 1 × 10^{-8} cm^2 V^{-1} sec^{-1} (much lower than the values quoted by van Beek, viz., 0.26 cm^2 V^{-1} sec^{-1} for powders[304] and 6 × 10^{-3} cm^2 V^{-1} sec^{-1} for single crystals;[307] the value quoted by Thomas and Clarke is incorrect). An estimation of the charge-carrier concentration suggests that only one in 10^{11} of the protons participate in the conduction process. Finally, while Thomas and Clarke discuss a proton-transfer mechanism for the conduction, the very low conductivity and mobility found do not, perhaps, preclude an interstitial proton motion through channels in the b direction.

The diffusion of tritium through lithium sulfate monohydrate has been examined[193] and found to be essentially temperature independent; i.e., a zero activation energy is reported. The diffusion process clearly operates by a different mechanism from the conduction process.

Lithium hydrazinium sulfate (LHS), $Li(N_2H_5)SO_4$, has been described as ferroelectric up to 437 K (164°) because of the presence of dielectric hysteresis loops. However, a number of properties show no evidence for a ferroelectric phase transition; for instance, there is no dielectric anomaly up to 205°, proton ^7Li nmr spectroscopy yields equivocal results in this respect, and chemical etching of the polar crystal shows no reversal of the etching behavior on application of fields an order of magnitude greater than the published coercive field (2500 V cm^{-1} as compared to 320 V cm^{-1}). On these accounts, it is concluded that LHS is not ferroelectric.[308]

The crystal structure[309] of LHS consists of an $LiSO_4^-$ framework containing channels running along the c direction. The NH_3^+–NH_2 ions lie in hydrogen-bonded chains within these channels, with one of the protons from the NH_2 groups involved in a hydrogen bond chain, $\cdots NH \cdots NH \cdots$, the other weakly bonded to a neighboring oxygen. The NH_3^+ groups do not participate in the hydrogen-bonded chain, but hydrogen bond to neighboring oxygens in the $LiSO_4^-$ framework. The neutron diffraction results show that the hydrogens (or deuterons) are largely in ordered positions relative to the framework.[310] Calculations and comparison with experiment suggest that the bias field maintaining this order is so high that there cannot be much dynamic disorder associated with the protons in the hydrogen bonds, and suggest that the unusual dielectric properties arise from a partially blocked protonic conductivity.[308]

Pepinsky, et al.,[311] first noted a high conductivity which obscured hysteresis loops above 80°; nmr evidence of highly mobile proton species led Cuthbert and Petch[312] to suggest a proton conduction process based upon proton transfer. Vanderkooy, Cuthbert, and Petch[313] examined the conductivity of single crystals of LHS from room temperature to about 200°. Dc conductivity was measured using an unguarded, two-electrode system along the three crystallographic directions, and the c axis conductivity (the direction containing the hydrogen-bond chain) was found to be some two orders of magnitude larger than in the a and b directions. Rapid initial decay of the current was noted (over a few seconds), followed by a much slower polarization; the conductivity data refer to results obtained after the initial current decay. The conductivity along the c axis was

$$\sigma/\text{ohm}^{-1}\,\text{cm}^{-1} = 49 \times 10^4 e^{-19.6\text{kcal mol}^{-1}/RT} \quad t < 160°$$

Ac conductivities (20 Hz to 5 kHz) were found to be an order of magnitude greater than the dc conductivities. Similar, or even greater, differences are reported by Schmidt, et al.[308]

At temperatures greater than 160° the c-axis dc conductivity decreases until, at 200°, the conductivity is nearly isotropic. This anomalous behavior appears to be due to a surface decomposition of the LHS. Electrolysis experiments[185,313] along the c axis yielded hydrogen gas in proportions according to Faraday's law assuming proton conduction. Generally similar electric properties are reported for deuterated LHS.[314]

The dc and dielectric properties of LHS have been studied rather intensively by Schmidt, et al.,[308,315] using a guard-ring procedure, who find lower dc conductivities than the values discussed above, but the same general room-temperature pattern. They, however, find the activation energies for a- and b-axis conduction to increase at higher temperatures, so that the conduction is almost isotropic above 200°. This apparent discrepancy from Vanderkooy, et al.'s, observation[313] is not commented

upon. The impurity concentrations of the single crystals were found to be rather high, about 1% for all impurities taken together.

The dc and rather complex dielectric data are interpreted on the partially blocked, one-dimensional proton conducting model mentioned above.[256b] In general terms, local defects within the channels reduce the conductivity while low barriers between channels, also caused by defects, permit diffusion between channels. Qualitative agreement between this model and the experimental results is obtained. It is noted that the dielectric properties at low fields cannot arise from the NH_2 and NH_3^+ rotations observed by nmr[314,316] since such rotations are to electrically equivalent positions and would not give rise to dielectric absorption. Similarly, the structural evidence is against total reversal of the $\cdots NH \cdots NH \cdots$ chain orientations.[317]

Hydroxides and Oxyhydroxides (see also H_xWO_3, section IV,A.1.a). There is considerable technical and fundamental interest in the thermal decomposition of hydrous materials, and the mechanisms of such processes are frequently discussed in terms of independent proton motion (as opposed to motion of water molecules or hydroxyl groups[17,18,318]). The oxyhydroxides, MOOH, compounds of certain trivalent metals,[69] have an α structure in which there are channels of independent $O—H \cdots O$ bonds (analogous to the bifluoride ion, $F \cdots H \cdots F^-$) and a γ structure containing a linked zig-zag chain of $\cdots O—H \cdots O—H \cdots$ bonds. Exchange studies show that the oxygen ions are not free to exchange, but that there is a rapid and free exchange of protons in both types of structure.[319,320] A proton exchange process for α-FeOOH has been proposed based upon making and breaking of hydrogen bonds down a channel to create a cooperative transfer sequence.[321] No electrical measurements have been made on this system, however.

An extensive study of the proton mobility, by ir, nmr, diffusion, and dielectric techniques, has been performed on γ-AlOOH (boehmite) by Fripiat and colleagues;[103,322-324] all the work reported has been performed on powders because it has not been possible to grow single crystals. The ir studies are somewhat equivocal and yield broadened absorption bands at high temperatures which may be due either to proton delocalization by tunnelling across hydrogen bonds, or to the anharmonicity of the proton vibration.[322,325,485] The dielectric results[323] are complicated, but indicate increasing conductivity with rising temperature, together with a dipolar absorption with an activation energy of 15.7 kcal mol^{-1}. The activation energy for diffusion has an almost identical value, according to Fripiat, *et al.*,[323] but Wei and Bernstein[319] report a lower value of 12.9 kcal mol^{-1} (not noted by Fripiat, *et al.*). Nmr measurements[324] (-145 to $+350°$) yield one broad and one narrow signal. The narrow band, indicating a population of delocalized protons, is not due to hydration water, is less intense in better crystallized materials, and is independent of specific surface area. However, it disappears on cooling below $-145°$. The activation energy of the process involved depends upon temperature but is about 2 kcal mol^{-1}.
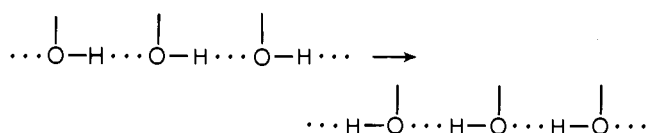
The observations are interpreted on a proton delocalization model. Ionic defects are formed rather than orientational defects because of the short hydrogen bond, with an activation energy of 10.6 kcal mol^{-1} (as determined from the difference between the activation energies for ac conductance and dipolar absorption). These ions then move through the hydrogen bond chain by a cooperative proton transfer process. MacKenzie[326,486] has recently developed this model, as a result of observing increased

dehydroxylation rates (in kaolinite) under dc fields. He conceives the proton transfers to be limited at the higher temperatures by oxygen vacancies in the structure; at such a vacancy the transfer chain will be broken until the OH_2^+ at the end of the transfer chain can hop into the vacancy. Support for this idea is found in the low relaxation rate found from the dielectric absorption, some 10^8 to 10^{10} sec^{-1} lower than for the proton transfer rate, with a higher activation energy than is expected for proton transfer across the hydrogen bond. An exotherm at $980°$ in kaolinite appears at up to $15°$ lower temperatures in the presence of electric fields.[486] This temperature reduction is accompanied by a mass loss, and the effects are accounted for by electrolytic removal of residual protons which aids the collapse of the metakaolinite structure to a spinel structure.

The hydrated nickel hydroxide electrode is used in the commercial nickel–cadmium battery, and there is consequently some interest in its mode of action. Lukovtsev[327] has proposed a redox mechanism in which, during oxidation, an electron transfer occurs at a nickel ion site in the $Ni(OH)_2$ which converts the nickel to $Ni(III)$ (*i.e.*, NiOOH) and releases a proton. Proton diffusion occurs through the structure to the electrode–electrolyte interface, where the proton reacts with an hydroxyl ion to form a water molecule. Lukovtsev and Slaiden[328] have reported rough values of the diffusion coefficient, while isotopic tracer experiments have shown that proton exchange with the solution occurs together with very little oxygen exchange. MacArthur[329] has measured the proton diffusion coefficient rather carefully by a potential sweep experiment and, assuming the above mechanism, quotes values of the diffusion coefficient of about 5×10^{-9} cm^2 sec^{-1} at room temperature, with an activation energy of about 2.3 kcal mol^{-1}. Feitknecht, *et al.*,[320] have also measured these parameters, by a radioactive tracer technique, where they measured the rate of exchange of hydrogen with water vapor. They find a combined enthalpy of proton defect formation and diffusion of 23 kcal mol^{-1} above $100°$, but no temperature dependence at lower temperatures, perhaps due to a change in the mechanism of defect formation.[330]

The thermal decomposition of brucite, $Mg(OH)_2$, is a matter of some controversy[318,331] because of the proposal of what is termed the inhomogeneous mechanism, whereby protons and Mg^{2+} ions migrate in opposite directions during the decomposition. Dielectric loss tangent data,[332] as a function of temperature increases (leading to decomposition) have been described by treating the protons, defect or excess, as lying in a conduction band with a mobility which decreases with rising temperature due to the increasing lattice vibrations.

ii. Molecular Materials. Alcohols. Certain molecular liquids freeze to a solid in which the translational freedom is lost, but not the rotational; such a "rotator" phase will have a high dielectric constant at sufficiently low frequencies if dipole reorientation is involved in the rotation. If reorientation of a hydrogen-bonded chain can occur

$$\cdots \overset{|}{O}-H \cdots \overset{|}{O}-H \cdots \overset{|}{O}-H \cdots \longrightarrow$$

$$\cdots H-\overset{|}{O} \cdots H-\overset{|}{O} \cdots H-\overset{|}{O} \cdots$$

the dielectric constant will be correspondingly higher, and proton conduction will accompany the reorientation if charge transfer can occur at the same time.[42,64,65,67]

Such processes are considered for the alcohols discussed below.

Alicyclic Alcohols. Both cyclopentanol and cyclohexanol have a complex phase behavior with a relatively high zero-frequency conductivity (the latter determined by extrapolation of the dielectric loss curve to zero frequency). Corfield and Davies[333] investigated this behavior for cyclopentanol in some detail and ascribed the conductivity of the high dielectric constant second phase (stability range of phase II: -37 to $-72°$) to a proton conduction process along a linear hydrogen-bonded chain. The activation energy for the conduction is about 9 kcal mol^{-1}. More recent investigations[334,335] have shown that both the high-temperature rotator phases I and II are characterized by short hydrogen-bonded chains, about three hydroxyl groups long. In phase I, the dipole moment of a chain is not constrained to point in any particular direction, but in phase II, in an order–disorder transformation, the dipole moments of the chains tend to be aligned parallel to the crystallographic c axis, without the formation of extended hydrogen-bonded chains.

While this new description of the dynamic behavior of cyclopentanol does not exclude proton conduction it would suggest an impeded proton flow, for the proton could not be transferred along a preexisting chain (*cf.* the discussion on secondary aliphatic alcohols, below). It must be noted also that, in the earlier report,[333] the measured conductance for cyclopentanol was less than that for cyclohexanone where no hydrogen-bonded chain could be expected and the latter also displayed an electrode polarization, while the cyclohexanol used was estimated to contain 7.3 mol of water per 1000 mol of cyclohexanol. Furthermore, the measured conductivity refers to zero frequency rather than to direct current measurements, and the two may not be identical.[66,337] Further experimental work is thus required before the proposed proton conduction scheme can be accepted.

Long-Chain Aliphatic Alcohols. The structural and dielectric results for alcohols described below have been fully reviewed[42,64-66] and are only given in outline.

Aliphatic long-chain secondary alcohols[66] have a high temperature form, usually obtained by crystallization from the melt, and a low-temperature form obtained by crystallization from a solvent. In both of these phases, the molecules lie parallel to one another, rather like the molecules in the corresponding paraffins, with hydrogen bonds extending on planes approximately normal to the axes of the paraffin molecules. The high-temperature form has a dielectric constant and loss at low frequencies which is more than ten times larger than that which would arise merely from molecular or individual dipole rotation, and is not displaced to lower frequency by increase in molecular length, so that it is associated with the hydrogen-bonded chain of hydroxyl groups. This chain is believed to be flawed, and the reorientation observed in the dielectric experiments is that of short chains of hydrogen bonds. The dc conductivities of these secondary alcohols are low.

The long-chain primary alcohols crystallize in a similar fashion, but joined end-to-end by hydrogen bonds which extend in a plane approximately normal to the molecular chains, with the oxygen atoms forming two parallel planes on either side of the plane of hydrogen bonds.[71]
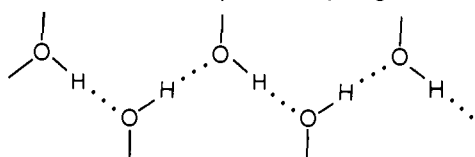
The phase behavior is somewhat complex but, briefly, they crystallize from the melt in a waxy, translucent α phase (characteristic of a rotator phase in the paraffins, and referred to as a gel phase by Piekara[342]), and later change to a more stable β phase.

These long-chain primary alcohols (impure C_{12}, and pure C_{14} to C_{26}—even values only) have a large dielectric absorption, but, in contrast to the secondary alcohols, they display as well a large low-frequency dielectric loss and a substantial dc conductivity.[42,64,336,337] The nature of this conductivity is discussed below with respect to cetyl alcohol, on which it has been most closely studied. Similar results with considerable dielectric absorption and conductivity have been found for the monoglycerides 1-monopalmitin and 1-monostearin in their α phases.[212,338] A proton transfer facilitated by molecular rotation has been proposed for the process. Dielectric results similar to those for the primary long-chain alcohols have recently been reported[339] for the primary alkoxyethanols, $C_nOC_2H_4OH$, and the primary alkoxypropanols, $C_nOC_3H_6OH$ (where $n = 16, 18, 20,$ and 22). The results were interpreted in terms of molecular rotation in the α phase, but their conductivities were not considered.

It should be noted that similar low-frequency absorptions to those described above have been observed in a variety of slightly conducting solids which, however, do not contain hydroxyl groups.[340,341] This absorption is probably of the Maxwell–Wagner type, resulting from macroscopic inhomogeneities in the sample; thus, solid dioctyl adipate with 0.4% of nitromethane deliberately added and also crystalline glycerol containing added water show similar dielectric behavior (the latter system at temperatures above its eutectic point).[341] These results reaffirm that it is necessary to study conductivity results directly before a conduction scheme should be described, for dielectric results (as an example) taken alone can be misleading.

Cetyl alcohol, $CH_3(CH_2)_4CH_2OH$ (1-hexadecanol), displays the general characteristics of a long-chain primary alcohol in the crystalline phase, as described above, with a dc conductivity[342] of about 1×10^{-8} ohm^{-1} cm^{-1} at $40°$. Kakuichi, *et al.*,[343] electrolyzed a sample of cetyl alcohol, at a temperature between its melting and transition points (about 40 and $50°$, respectively), in an evacuated container and confirmed that hydrogen gas was evolved by spectroscopic identification of a discharge through the gas in the container. This appears to be the first reported identification of hydrogen as a product of a solid-state electrolysis.

Recent work tends to confirm the earlier results although the conductivities measured with guard rings[127] are much lower, about 5×10^{-11} ohm^{-1} cm^{-1} at $40°$. The bulk conductivity rises very steeply with temperature, through three orders of magnitude in the α phase, and then falls some two orders of magnitude when melting occurs.[342] Using a Pd|H electrode, the conductivity was found to be ohmic and very time-dependent in the temperature range of the α phase.[127] These results are interpreted in terms of proton conduction by a cooperative transfer process in the α-phase, while in the low-temperature phase there may be the formation of closed chains of hydrogen bonds (tetramers, for example) which will not show a high polarization or a high conductivity. The same lower transition point is also found, at unaltered temperature, in quite dilute solid solutions of cetyl alcohol in benzene and in hexane; this seems to suggest that the lower transition is independent of hydrogen-bonded chain length and so may arise from the breakdown of such chains and the formation of closed multimers. The

relatively low conductivity of the liquid is ascribed to the reduced order in that state and to a less favorable placement of oxygen atoms to permit molecular rotation.[342]

1-Tetradecanol. An electret is a more-or-less permanently electrified body having electric charges of opposite sign at its extremities, often prepared by allowing a liquid to solidify in a strong, static electric field.[29d,418] A wide variety of materials, among which is 1-tetradecanol,[344] is found to form electrets. It has been found that the volume polarization in 1-tetradecanol is caused by a distribution of space charges, with the negatively charged species having the higher mobility since it is mobile at lower temperatures. Deuteration of the hydroxyl group does not affect the electret property significantly. On these counts a proton conduction process is not favored for 1-tetradecanol, and it is believed that the behavior may be ascribed to the passage of impurity ions. It should be noted that these measurements were performed at low temperatures generally, and all below 30°, while the transition temperature[42] for 1-tetradecanol is 34.4°. Thus, the conclusion against proton conduction appears to refer only to the crystalline β phase, in common with the conclusion for other long-chain primary alcohols.

b. Sheets of Hydrogen Bonds

i. Cupric Formate Tetrahydrate. Cupric formate tetrahydrate, $Cu(HCOO)_2 \cdot 4H_2O$, is antiferroelectric below 234 K ($-39°C$) and antiferromagnetic below 17 K. The structure[345-347] is layer-like, with a prominent cleavage. The water molecules, in two nonequivalent forms, are sandwiched between copper formate layers and hydrogen-bonded within planes; there is proton disorder within the hydrogen bonds in the paraelectric phase.[345-348]

Although dc conductivity measurements have not been performed, dielectric[349,350] and nmr[351] measurements indicate proton conduction along the plane of water molecules. Below the phase transition at about $-39°$ there appears little dielectric absorption.[349] Above this transition there is a large increase in the radiofrequency permittivity parallel to the cleavage plane and only a small increase perpendicular to it. This change is ascribed to the onset of rotation of the water molecules, which conclusion is supported by the nmr data. The activation energies of these dielectric relaxations are about 6 kcal mol^{-1}. No more direct evidence for proton conduction in this material is available. Giesekke[352] has prepared protodes for use in conductivity measurements on this material, but finds no reproducible injection effects.

ii. Normal Aliphatic Carboxylic Acids. The normal aliphatic carboxylic acids, $CH_3(CH_2)_nCOOH$, form closed dimers, and, for the long-chain acids, these dimers tend to crystallize so that the hydrogen-bonded groups lie in a plane with the chain axes parallel.[71] Thus there is a plane in which proton-transfer processes may occur; this is not, of course, a linked plane of hydrogen bonds, but rotation of the molecules about their axes, as is possible with paraffinic systems, may promote highly anisotropic conductivity. Two examples are discussed.
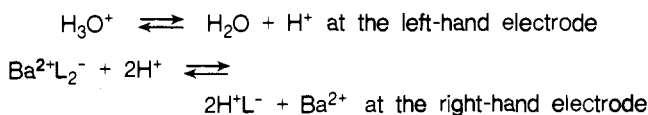
Stearic acid, $CH_3(CH_2)_{16}COOH$ (octadecanoic acid), has received some attention insofar as its electrical properties are concerned, partly because it can be prepared in multimolecular-layer films. The conductivity is believed to be electronic,[353] although an early study[343a] suggested proton conduction.

Lauric acid, $CH_3(CH_2)_{10}COOH$ (dodecanoic acid), was utilized by Shedlovsky[354] in an ingenious fashion, to form a "protochemical" cell with "protodes." Using HL to rep-

resent solid lauric acid, and BaL_2 for barium laurate, the cell is

glass electrode|solution: H_3O^+, Ba^{2+}, Cl^-|BaL_2, HL
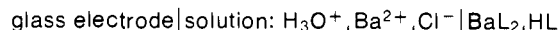
This cell involves proton exchange rather than electron exchange, and the protochemical cell reaction postulated is

$$H_3O^+ \rightleftharpoons H_2O + H^+ \text{ at the left-hand electrode}$$

$$Ba^{2+}L_2^- + 2H^+ \rightleftharpoons$$
$$2H^+L^- + Ba^{2+} \text{ at the right-hand electrode}$$

so that the cell should be sensitive to pH and to the Ba^{2+} ion activity. The connection to the external circuit was completed with Ag,AgCl electrodes dipping into similar buffered barium chloride solutions of various concentrations, in contact with the glass electrode and with the mixed BaL_2, HL. Nernst's law was found to be accurately obeyed for this cell for a pH range of 1 to 8 and a barium concentration range of between 1 and 0.005 m. The effect of the cell is to separate complementary acid and base reactions from one another, just as an electrochemical cell separates oxidation and reduction reactions, and Shedlovsky used the result to illustrate that a similar process could occur in biological systems, provided protonic conductors exist in such systems.

While the point is well illustrated, the result cannot be construed as proving that lauric acid is a proton conductor; it simply serves as an exchange medium reversible to both Ba^{2+} and H^+ ions, just as the glass electrode is reversible to protons, and internal ion transfer does not appear to be essential.

c. A Three-Dimensional Network of Hydrogen Bonds

i. Ice. Ice has become the model of a hydrogen-bonded system by virtue of its close, three-dimensional network of hydrogen bonds and because of its natural importance. The conductivity of ice has been most extensively studied and analyzed, and descriptions of proton conduction processes are generally couched in terms derived from discussions devoted to ice. Nevertheless, the details of the conduction process and even the nature of the charge-carrier in ice are by no means finally settled, while ice is in many ways a unique "proton dielectric,"[377] with its exceedingly high proton concentration, its various hydrogen-bonding networks in its many different phases, and since most experiments on it have been performed in a temperature range rather close to its melting point, where unusual surface[359c] and premelting phenomena may interfere with the property being investigated. Thus, while ice must retain its importance in the field, its unique properties cannot be invoked incautiously in explanation of the properties of other proton conductors. The relationship between the protonic conductivity of ice and of biological materials has been extensively discussed, especially by Riehl.[271,423]

The literature on the electrical properties of ice is exceedingly large, but will not be extensively examined here because of the existence of a number of recent reviews; rather, the presently understood position will be presented with discussion of a number of more recent and important papers so that the reader may be brought up to date in the field. Any report on reviews of the electrical (and other) properties of ice must commence with the extensive compilations by Dorsey (1940)[355] on the properties of ice and of liquid water, and by Pimentel and McClellan on hydrogen bonding (1960 and 1971);[12] more recent reviews are the book by Eisenberg and Kauzmann

(1969)[356] on ice and liquid water, Glen's paper on structure and point defects of ice (1969),[357] Fletcher's book (1970) on the chemical physics of ice (with an extension on ice structure in 1971),[358] while two recent (1972) books edited by Horne[359] and by Franks[360] are devoted to the properties of water and of ice, including chapters[359a,250a] dealing with the electrical properties. These texts are very comprehensively complemented by the proceedings of four International Symposia on the Physics and Chemistry of Ice (the first, 1962, in Erlenbach being unpublished, the second in Sapporo,[361] the third in Munich,[362] and the most recent in Ottawa[363] in 1972). A comprehensive bibliography on the properties of ice appears in each issue of the *Journal of Glaciology*.

Almost all the significant conductivity work on the ices has been done on ice Ih, the hexagonal form stable at atmospheric pressure and at temperatures below 0°; in what follows, the term "ice" will be used to refer to ice Ih. Ice Ih has a würtzite crystal structure[72c,359b] analogous to that of the tridymite modification of SiO_2; each oxygen atom is tetrahedrally coordinated to four other oxygens at 2.75 Å, the oxygen atoms being arranged on two interpenetrating hexagonal close-packed lattices. The hydrogen atoms lie at 0.99 Å from an oxygen atom more or less between two oxygen atoms but not necessarily on the O⋯O line. The hydrogen atoms are coordinated randomly to their adjacent oxygen atoms according to the Bernal–Fowler rules,[364] which specify that the water molecule remains essentially intact in ice so that, of the four bonds connecting an oxygen, only two contain a proton at a short distance (specifically, at 0.99 Å as determined by experiment), and each bond contains exactly one proton. These rules permit some randomness in the structure, for they do not specify along which of the four bonds the more closely coordinated hydrogen atoms lie. The randomness was confirmed by Pauling's evaluation of the residual entropy of ice[365] (refined by Nagle[366] and Suzuki[361a]) which has almost exactly the value (R ln 3/2) that the disorder permitted in the Bernal–Fowler rules yields, and by neutron diffraction on heavy ice (D_2O)[367] which depicts the structure as having two half-deuterons along each O⋯O bond; there is assumed to be a statistical distribution of the deuterons over the pairs of positions available to them, closer to one or other of the oxygens between which they are bonded. There are suggestions that, at low temperatures, ice may form an ordered ferroelectric phase.[363a,368]

Mechanism of Conduction and Polarization in Ice. The static permittivity of ice ($\epsilon_0 = 95$ at $-10°$) is comparable with that of liquid water ($\epsilon_0 = 78.2$ at 25°) but with a much lower relaxation time (6×10^{-5} sec for ice at $-10°$, compared with 17.67×10^{-12} sec for liquid water at 0°), while both are ascribed a single relaxation time, rather than a distribution of relaxation times.[359a] This high permittivity of ice requires molecular reorientation processes to occur which are inexplicable in the ideal crystal. Standard solid-state concepts would suggest the reorientation to occur, then, by the transfer of a proton across a hydrogen bond, to form a pair of ionic defects, OH^- and H_3O^+.

$$2H_2O \; \rightleftharpoons \; OH^- + H_3O^+$$
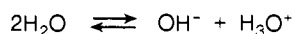
Bjerrum[369] noted that the migration of such ion states through a sample of ice will lead to the formation of a dipole moment in the chain of molecules through which migration had occurred which is in the *opposite* direction to that corresponding to the proton jumps and, on a rough electrostatic picture, larger than the latter; hence, the

molecular turns at the ions could not explain the dielectric properties of ice. However, the orientational faults which have previously been introduced could be used in explanation of the dielectric behavior. These are the D defect, in which two protons occupy a single hydrogen bond, and the L defect, in which no protons lie between the oxygen atoms, both in violation of the second Bernal–Fowler rule. Such defects may be conceived as arising from the rotation of a water molecule in the ice lattice, pivoting about one of its hydrogen bonds through the 120° required to permit it to re-form bonds to neighboring oxygens. After the rotation one of the former bonds will have lost a proton, to form the L defect, while another will have gained that proton, to form a D defect. Once having formed, such orientational defects may migrate separately by rotations of the adjoining water molecules, and so imprint a polarization in the expected orientation on the ice lattice. Conduction proceeds by the movement of the ionic defects, OH^- and H_3O^+; their motion polarizes the chain of hydrogen bonds through which they have passed and no further conduction can occur unless the chain is reverse polarized by the motion of the appropriate orientational defect down the chain. The orientational defects are regarded as being in much higher concentration than the ionic defects, thus ensuring that the majority of conduction chains remain available for proton transfer processes.[370] Experimental evidence for this conclusion is provided by results of systematic impedance measurements[371] on samples containing varying amounts of dissolved HF (which is believed to replace H_2O, creating an L defect at the site of the replacement); these measurements show that conduction is aided by the introduction of additional protons, but the dielectric relaxation is not much affected until the dc conductivity reaches the order of magnitude of the high-frequency ac conductivity.[359a,370]

Recent experiments have cast some doubt on the validity of this analysis. Firstly, it is not necessarily true that HF is dissolved substitutionally in the ice lattice, and at higher concentrations it (and other impurities as well) may segregate in the ice structure,[363b,372]—perhaps in grain boundaries—so that theories which rely on a uniform distribution of the impurity may have to be reconsidered. Furthermore, while more recent experiments have tended to confirm the general pattern of the conclusions[359a] (leaving aside the problem of possible segregation), some of the details are not confirmed. Thus, at temperatures below 218 K, Camplin and Glen[363c] find that σ_∞, the limiting high-frequency conductivity corresponding to ϵ_∞, increases approximately as the square root of the HF concentration rather than proportionally as required by the theoretical analysis. This square-root dependence is explained by association of the extrinsic ionic defects at low temperatures.

The movement of a Bjerrum defect may be adequately described in terms of the rigid lattice model implied above, where the faulted bonds are unaltered except for the presence or absence of a proton; a more realistic model would, however, allow for relaxation of the lattice about the defect,[373] or the combination of the defect with other types of solid-state defects, such as interstitials[374] or vacancies.[362c,370] The D defect, in particular, will have an excessive energy on the rigid lattice model because of the repulsion between the adjacent protons, and the possibility of a rotated D defect has been discussed.[375] Such detailed models of the Bjerrum defects are briefly reviewed by Gränicher[362a] and by Jaccard.[359a]

The majority of discussions since 1951, on the electrical and transport processes in ice, have been couched in

terms of the Bjerrum orientational defects[359a,362b,370,376] but, rather recently, von Hippel and coworkers[363d,e,377] have reported on an extensive series of investigations on ice, and have seriously questioned the now-conventional Bjerrum interpretation. von Hippel[377b] has considered whether there may be a mechanism for the transport properties of ice which is unique to ice, rather than the generalized mechanism inherent in the Bjerrum model which can be (and indeed has been) rather straightforwardly adapted to the description of the proton conduction mechanism in other chain hydrogen-bonded solids. von Hippel accepts the Bjerrum orientational defects as the basis for his model, but describes a pair of L and D defects as arising by a direct proton transfer from bond to bond, occurring rather naturally during the vibrations of a water molecule, rather than by the excessively energetic process of breaking three hydrogen bonds followed by molecular rotation about the remaining bond. Then, rather than regarding the L and D defects, once having been formed, as independent, von Hippel considers that they give rise to the dielectric polarization by a field-induced drift apart, and die by recombination with counterdefects, similarly generated by thermal processes. The correlation time, related to the dielectric relaxation time, is the statistical waiting time until the same H_2O molecule is triggered into rotation again.

von Hippel's description of the conduction process is a much more radical departure from precedent; he finds it unnecessary to assume intrinsic conduction by OH^- and H_3O^+ ions, but rather invokes the conversion of L or D defects at the electrodes into OH^- and H_3O^+ ions, with the eventual formation of gas (O_2 or H_2) at the anode and cathode, by an appropriate sequence of reaction. von Hippel's principal objection to the concept of ion migration in ice is that such migration "stretches an antipolarization chain in the ice lattice from cathode to anode, *which pumps the corresponding charge again upstream. The result is no current flow.*" While this effect of antipolarization must be acknowledged (and was, indeed, recognized by Bjerrum), the contribution of this chain to the effective current seems to have been overstated by von Hippel.[363f] Onsager and Dupuis[370c] have estimated the effective charge of an orientational defect as being about 2×10^{-10} esu, which is less than half a free electronic charge (4.8×10^{-10} esu); the migration of such a defect down a chain will reverse its polarization. Therefore, the effective current flow due to ion migration may be reduced by the antipolarization, but it is not nullified. While von Hippel discounts intrinsic ion migration in ice, he acknowledges its contribution to extrinsic conduction. von Hippel's principal conclusion, which is based on what appears to be an inadequate argument, is that "ice Ih single crystals are not proton semiconductors; on the contrary they seem to be insulators until the single-crystal status is destroyed."

Experimental Measurements of Conductivity on Ice. The first conductivity measurements on ice appear to be those of Ayrton and Perry,[378] and there is a long line of work which proceeds therefrom; the first reliable quantitative result is that of Johnstone,[379] who used a four-probe method to determine that the conductivity follows an Arrhenius law, with a value of 10^{-10} ohm^{-1} cm^{-1} at $-10°$. More recently, important conductivity work has been reported by Gränicher and coworkers at the ETH, Zurich, by Eigen, de Maeyer, and coworkers of the Max-Planck-Institut, Göttingen, by Riehl and coworkers at the Technischen Hochschule, Munich, and by von Hippel and coworkers at MIT, Cambridge, Mass., while a number of other groups have also worked on the problem. The principal early dielectric work was by Auty and Cole (1952),[380] more recently followed by Wörz and Cole,[362d,381] as well as by many reports from most of the groups mentioned above together with a number of other groups.

In the late 1960's, knowledge of the conduction properties seemed to be fairly well established.[356,359a] The ionic nature of the conductivity had been confirmed by electrolysis, which yields hydrogen at the cathode and oxygen at the anode,[382] by mass transport (in impure ice),[383] by emf measurements,[384] by space-charge injection,[385a] and by Hall effect measurements.[385b] Conductivity measurements were rather seriously interfered with by electrode polarization, but this was recognized and precautions against it were taken by using four-probe methods or by using protodes of various sorts; these protodes yielded the expected enhancement in the conductivity and were thus assumed to act as ohmic electrodes.[362e-g,386] The activation energies thus determined varied, however, quite considerably among the various workers, even though considerable care was taken; values of the activation energy for dc conduction from 0 to 46 kcal mol^{-1} were reported by different authors.[377] These activation energies seemed to converge toward the 13.1 kcal mol^{-1} determined by Eigen, de Maeyer, and Spatz,[387] who measured saturation currents in ice (by applying high fields). The saturation currents were assumed to arise from the ionization of the water molecules in the ice, so that the rate constant for the ionization and the charge-carrier concentration could be determined. However, careful investigation of the surface conductance showed that it is considerably higher than the bulk conductance near the melting point of ice, at which temperatures most measurements are performed; this causes significant distortion of the potentials within the crystal so that even four-probe conductivity measurements with apparently ohmic electrodes yield unsatisfactory data.[362e,f,388] Furthermore, while the necessity for pure, near-perfect crystals was appreciated, ageing effects have now been noted[363g,h,m,377c] as arising from the strains induced in the crystal while growing from water or being worked.[363l] These effects also arise during the freezing of dilute aqueous solutions, when charge separation and static electrification may occur (Costa-Ribeiro or Workman–Reynolds effect).[358] Schneider, *et al.*,[363i] and von Hippel, *et al.*,[377] have pointed out that the electrical history of the ice sample may also affect the parameters which are being measured, so that adequate rest periods for recovery must be allowed between measurements. Finally, in these measurements a decreasing current with time at constant applied voltage has often been observed; it was uncertain which value of the current was characteristic of the sample—a final, steady value, or a value determined after a fixed (short) time interval, or a value extrapolated back to zero time (*cf.* section II.C.1). Measurements, too, were generally made with instruments having a characteristic response time of the order of sec, so that any faster changes were, in fact, obscured. These points of difficulty are discussed in more detail by Engelhardt, in an excellent review paper.[363j]

Very recent work has attempted to remedy these defects by using highly controlled procedures. The first precaution was elimination of the effects of surface conduction by use of guard rings around the measuring electrodes.[362e,f,389] This confirmed that the bulk conductivity is indeed much lower than the surface conductivity, and that there is a much faster time decay of the bulk currents than of the surface currents. This decay arises from space-charge buildup at the electrodes due to impeded

charge-carrier discharge, which also seriously distorts the fields inside the crystal so that applied and effective fields may vary widely in time and in position in the crystal. Potential probes were applied to measure the internal field in the ice crystal;[362e,f,388] these probes were guarded by auxiliary rings whose potential could be brought to that of the probe, so removing surface perturbation of the potential measured by the probe. A number (up to four) of belt electrodes were frozen around the ice cylinder, and these were adjusted to the volume potential to eliminate radial field components. Finally, measurements have been made over a wide frequency range[363i,377] from the mega- to the millihertz region, with varying pressure,[363k] to yield a full spectrum of the electrical behavior of ice.

The transient responses of cylindrical ice crystals were examined with the precautions described above,[363i] and it was found that the potential along the cylinder axis rises to the anode potential in a few seconds. Such an asymmetric potential distribution cannot arise from orientational polarization of the ice molecules, such as would occur in the absence of ionic defects, and must imply an ionic (i.e., protonic) conductivity, with the ions being unable to discharge at the cathode. This observation accords rather well with the results of a random walk computation by Babcock and Longini,[376] assuming mobile positive charge-carriers only. It is suggested[363j] that electrons leave the crystal at the anode, discharging negative ions and freeing positive charges which move across the crystal until they are blocked at the cathode. It is concluded that, until a truly ohmic (protonic) cathode is developed, the true dc conductivity cannot be measured; consequently, it is believed that earlier Hall effect measurements,[385b] on ice are invalidated by the polarization and surface conduction which must have occurred. The transient experiments[363i,j] yield activation energies for dc conduction of about 2.6 kcal mol^{-1}, and for ac conduction of about 13.4 kcal mol^{-1}, both at $-10°$ and for both H_2O and D_2O ice. The ac conductivities at this temperature are about 10^{-7} ohm^{-1} cm^{-1} for both ices, but the dc conductivities are very different, at 3.0×10^{-9} ohm^{-1} cm^{-1} for H_2O and 9.8×10^{-11} ohm^{-1} cm^{-1} for D_2O. These results are taken to indicate a thermally activated process for the ac measurements, but the isotopic influence indicates that a tunnelling process is involved in the dc conductivity. The ac and dc conductivity plots cross over below about $-50°$, indicating a change in mechanism whereby, at the lower temperatures, the Bjerrum orientational defects control the dc conduction while the ionic defects control the ac conduction.

On shorter time scales, by transient methods (Munich group)[363i,j] and by dielectric methods (MIT group),[363d,367e,377] a number of separate relaxation processes are discernible.[390] The Munich group was able to resolve four processes in ice by their transient (time-domain) methods while the MIT group has analyzed their frequency domain data into seven discrete processes. This latter sevenfold analysis, while within the experimental errors, must be regarded as something of a mathematical artifact without other evidence to justify each relaxation, for the analysis was performed assuming each relaxation to be a strictly Debye process, having no distribution about the single relaxation time, while the low-frequency spectra are necessarily observed in the space-charge polarization time scale; hence, only the four higher frequency spectra are to be regarded as well determined in a fresh crystal, but six in an aged crystal. Three processes are required if distributions are permitted.[363e] As mentioned earlier, the MIT group regards the hypothe-

sis of intrinsic proton conductivity as unnecessary in pure ice and ascribes their high-frequency relaxation spectra to processes dependent on defects (whether Bjerrum or Frenkel defects) and the lower frequency spectra to space-charge polarization processes.[363d] The behavior is seen to be exceedingly complex, and the present situation in ice crystal studies has been suggested to be akin to that pertaining in the study of alkali halide color centers some 50 years ago, so that much remains to be done.

Engelhardt[363j] has reported attempts to repeat the earlier saturation current experiments; he found only an effect in which increasing the field yielded a current which mimicked the saturation current and remained constant, but as a result of a balance between the increasing field and the increasing polarization and with a value very dependent on the electrode geometry. Thus it was not possible to separate the conductivity, by this method, into charge-carrier concentration and mobility terms. However, a mobility for protons of 10^{-3} cm^2 V^{-1} sec^{-1} at 150 K, increasing with falling temperatures to 118 K, has been determined by a transit time measurement of injected protons; such protons were created by flashing a laser pulse onto the hydrogen-saturated palladium anode surface.[363n] This value compares well with the 5×10^{-3} cm^2 V^{-1} sec^{-1} determined by the MIT group from their saturation charge measurements,[377] which yielded a measure of the extrinsic charge-carrier concentration in the crystal under study.

Self-diffusion in ice does not appear to be controlled by the proton transfer processes which are here discussed. Diffusion coefficient measurements[370a,391] indicate that oxygen and hydrogen diffuse at the same rate (2 to 3 $\times$ 10^{-4} cm^2 sec^{-1} at $-10°$, activation energy 14.5 kcal mol^{-1}),[358] suggesting that intact molecules are diffusing. Consideration[370a] of various defect combinations (e.g., a D defect plus an interstitial molecule) which would combine a displacement current with mass transport showed that such combinations move too slowly to account for the observed diffusion coefficient. It is thus concluded that diffusion is attributable to a process which is electrically (and mechanically) inactive, and that proton diffusion must make only a small contribution thereto.

Nmr has not played a large part in the analysis of the conduction process in ice, but the significant information which it can impart is being considered.[359d,363o,392] Recent results[393] which indicate a liquid phase in polycrystalline ice above about $-20°$ are particularly interesting in the present connection.

Theoretical Treatments of Conduction in Ice and Other Chain Hydrogen-Bonded Systems. Most of the available theoretical treatments of the conduction process in ice were published well before the new developments in the experimental situation, and therefore rely on the older, simpler results. While this detracts from the significance of their quantitative conclusions, it does not affect their basic, conceptual approach. Furthermore, the concepts of the conduction processes may be considered to apply not only to ice but also to other systems in which there are connected chains of hydrogen bonds along which the transfer of protons may be directed.

The detailed quantum mechanics of the proton conduction process has been treated by a number of workers.[80-89,362h,458] These studies commence with the basic assumptions of hydrogen bonding,[394] in particular that each of the protons in the bonds linking H_3O^+ to adjacent H_2O molecules move in a symmetric (or nearly symmetric),[81a,b] double-minimum potential well; the well is symmetric because the proton may be considered as

moving between two water molecules. Proton transfer across this well forces a proton in an adjacent bond along its bond, and so a correlated (and, therefore, highly efficient)[90] proton transfer process occurs. This process is particularly well illustrated by the system of connected springs used by Weiner and Askar[395] to illustrate their one-dimensional model of such a cooperative process as related to dislocation motion in a crystal.

. Gosar[80a] treated the protons, in the way described above, as localized in the potential wells of the hydrogen bonds and found a relatively complex relaxation mechanism involving two-phonon processes. The correlation of proton transfer is contained in the result as a mean free path for proton motion which is about three times the bond length. A correlated motion of the bond defects has also been discussed.[362i] This same model may be treated by a nonlocalized procedure where the protons (or H_3O^+ ions) are assumed to be associated with an energy band, as are electrons in semiconductors; the results of the two treatments are essentially the same. The first such analyses dealt with a one-dimensional case only, the mobility being limited by proton–phonon interaction.[80b,86] Kim and Schmidt[83b] have treated the mobile protons as classical point particles, with a quantized energy transfer between proton and lattice, to yield a reasonable mobility when both librational and translational modes of motion of the water molecules are taken into account. These weak proton–phonon coupling approximations are regarded as inadequate by Kubarev and Shedrin,[87] for the interaction energy of protons with phonons (estimated at 10^{-14} erg) is large compared to the proton band width (10^{-15} erg); therefore, they attempted a strong coupling analysis, following Gosar and Pintar's model.[80b] This yields a temperature dependence for the proton mobility of $T^{-3/2}$, instead of the T^{-1} dependence found by Gosar and Pintar.

Sussmann[81] has treated the same linear hydrogen-bonded system but has lifted the condition of a symmetrical hydrogen bond in order to obtain localization of the proton in one of the potential minima; such lifting of the degeneracy will result from minute perturbations, according to Sussmann. He, too, treats the mobility as being limited by proton–phonon interaction and obtains a non-activated mobility provided that the energy difference between potential minima is sufficiently small. Such a phonon (or other) interaction is indeed necessary for proton transfer in this model for, as Sussmann[81b] shows, proton transfer cannot occur in the absence of a time-dependent perturbation.[492] Furthermore, it is necessary to consider that the crystal may relax around, or accommodate, a transferred proton, so that an effective mass has to be used for the proton which may have a value very different from that of the free proton.

A rather different approach to a treatment of a three-dimensional (cubic) ice model has been taken by Minagawa.[458] The proton transfer among tetrahedrally bonded H_2O molecules is taken as being described by an energy band, and is thus coherent. No phonon interaction at all is considered, but the proton transfer is random among the three protons of an H_3O^+ ion, which results in a finite mobility for the proton transfer through the crystal. The energy band which results is rather narrow, suggesting that the three-dimensional proton motion should be regarded as restricted to motion along a collection of many one-dimensional bands. The mobility obtained (1.8×10^{-5} cm^2 V^{-1} sec^{-1} at $-10°$) yields a coherent proton transfer length of about four bond lengths. These results show a rather interesting correspondence with those of Gosar and Pintar.[80b]

Pinchukov[89] has attempted to treat the dielectric properties of ice by assuming a thermally activated proton transfer

$$HO-H\cdots OH_2 \rightleftharpoons HO^-\cdots {}^+H_3O$$

ground state   excited state
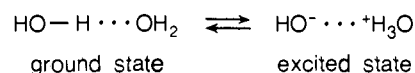
followed by further proton transfers which separate the ions. When straightforward and perhaps naive statistical mechanics, ignoring tunnelling, is applied to this system, an activation energy for the dielectric relaxation follows which is the same as the activation energy involved in the original proton transfer. On this account, Pinchukov questions the necessity for considering Bjerrum defects as contributing to dielectric relaxation in ice; he does not, however, discuss the conductivity of ice.

Calculations of the potential energy curves for the migration of ionic defects have been performed using a molecular orbital method[83a] and a valence bond method.[88] These calculations require a rather unrealistically low $O\cdots O$ distance to yield the early, high value of the proton mobility; this failing may be remedied by the lower values now ascribed to the proton mobility.

As mentioned earlier, these analyses are not solely applicable to ice, and should be considered in relation to proton transfers in other systems;[363f,81b] Kobayashi[84] has, indeed, attempted an analysis of a collective proton tunnelling mode in ferroelectric KH_2PO_4-type materials and in α-helical polypeptides (the latter system was chosen in preference to the intrinsically more interesting DNA because of the anticipated large asymmetry in the potential wells of the DNA). The possibility of occurrence of such a mode is partly suggested by the correlated breaking of hydrogen bonds in the helix–coil transition, in a zipper-like manner. It is shown that the sound velocity through proteins should increase on deuteration due to a decrease in the tunnelling frequency when there is a correlated collective proton mode, but that the sound velocity should decrease on deuteration in the absence of such a mode, simply due to the increased mass of the material. No tests of these conclusions have been published, it would seem.

ii. Adsorbed Water. Any attempt to review the dynamic properties of water adsorbed on various surfaces would be a large task in itself, and is regarded as being beyond the scope of the present review. A few of the more recent or relevant publications in this field will be mentioned for completeness, however.

Reviews of nmr spectroscopy of adsorbed water molecules have been published by Packer,[396] Resing,[397] and Fripiat,[103] while the dielectric observations on adsorption are discussed by McIntosh[398] and Davies.[67] Studies of the dielectric behavior of adsorbed water during dehydration of alums is reported by Hall and coworkers,[399] and on α-Fe$_2$O$_3$ by Zettlemoyer, et al.[400] Surface conductivity in some silicate materials is discussed by various groups and especially by Fripiat, et al., in a series of well-referenced papers.[101b,103] Extensively referenced reviews of the behavior of adsorbed water, including electrical properties, have been published by Drost-Hansen[401] and by Jellinek.[359c,402]

C. Organic Polymeric Systems

The electrical properties of organic polymers are of increasing interest, both due to their technical importance and to the interesting relation between such properties and their physical structures.[29,403-405] Their conductivities are low (with certain exceptions) and will generally

be considerably influenced by the presence of impurities; however, Pohl has argued[406] that the low permittivities of such systems will inhibit ionization and so reduce the contribution of ionizing impurities to the conductivity. For most polymer systems, the conduction will be an extrinsic, electronic process, but for a few systems where there is a large concentration of hydrogen bonds (or of oxygen atoms, to which interstitial proton transfer can occur) it seems possible that proton conduction can occur, either by a cooperative proton transfer process or by migration from oxygen to oxygen. No attempt will be made here to review the literature on proton conduction in polymeric systems, for this would increase the scope of this report too widely.[407] Brief mention will be made of systems in which protonic conductivity is believed to occur.

The most significant of extensively hydrogen-bonded polymeric systems is that of the polyamides (nylon).[42] Their high dc conductivity was first ascribed to proton conduction by Baker and Yager,[408] following a suggestion by M. L. Huggins, in what appears to be the earliest discussion of a proton conduction process in a solid material. The present position[409,410] is that the conduction is believed to be electronic below ~110°, but that there is combined protonic and electronic conduction above this temperature. This changeover in mechanism appears to be associated with the transition to the more mobile α-phase of the polymers, which permits the rotation which is required in the charge-transfer process.[410] (Egg albumen displays rather similar electrical properties to those of the polyamides.[411]) Polysulfinimides, $(SONH)_n$, are similarly extensively hydrogen-bonded, and electrical measurements indicate an ionic charge-carrier which is believed to be the proton, partly on the basis of the effects of water on the conductivity.[412] Polyglycine has a conductivity which is also markedly affected by water vapor, but the conductivity is believed to be electronic at water contents less than 3%, becoming protonic at higher water contents.[224,413]

Polyolefin oxides are not hydrogen-bonded but contain oxygen as a possible proton-accepting atom in the polymer chain. The conductivities[414] near the melting points (room temperature) of poly(ethylene oxide), poly(trimethylene oxide), and poly(tetramethylene oxide) are nine orders of magnitude higher than for other saturated organic polymers, and impurity conduction can be excluded. Thus, when the chain mobility is sufficiently high, proton transfer processes can occur, the proton passing from oxygen atom to oxygen atom by a handing-on mechanism. The electrical properties of "dipping" or "electrophoretic" lacquer under strong fields have recently been interpreted[415] in terms of a small degree of dissociation of carboxyl groups, followed by charge separation of the protons from those groups under the influence of the field. Similarly, poly(ethylene terephthalate), "Mylar," will contain small concentrations of hydrogen-bonded carboxylic acid end groups

$$-COOH \cdots O$$

These bonds may break and ionize to produce protons available as charge-carriers; while there is some discussion on whether the conduction mechanism is predominantly ionic or electronic, it would appear[416] that protons do contribute to the conductivity above 100°.

Polyelectrolytes are used as membranes in electrodialytic desalting processes and as solid electrolytes in fuel cells, while they also form electrets; there is thus considerable interest in their conductive properties. Even in very

dry polystyrene sulfonate membranes, ionic conduction is the predominant mechanism of charge transfer, and the ionic charge carriers are believed to be protons resulting from dissociation at the sulfonic acid sites within the membrane.[417,418] Similar results have recently been reported for dry phosphonic acid polymer films.[419]

D. Biological Systems, Including Biopolymers

The case for the contribution of proton conduction and transfer as a general energy- and charge-carrier mechanism in solid biological systems has been under discussion for a considerable period[14-16,420-422] with Riehl,[271,420a,423] Eley,[421a,422a,424,425] and Rosenberg[426,427] being among the principal contributors. The problem is compounded in biological systems because of the presence of water, adsorbed or free, in the natural state so that it is difficult to extricate the effects of the water from intrinsic effects within the biopolymeric system.[360,428] Reviews on conduction and proton conduction in a variety of biopolymeric systems, proteins,[426,429] nucleic acids,[430] and lipid membranes,[426,431] have recently appeared and the material will not be repeated here, except for a statement of the present position.

For dry proteins, a conductivity which rises with temperature is apparent; the room-temperature conductivity is less than 10^{-16} ohm^{-1} cm^{-1} and the experimental activation energy is about 25 kcal mol^{-1}, i.e., an activation energy of 50 kcal mol^{-1} on the basis of the semiconduction expression

$$\sigma = \sigma_0 e^{-E/2RT}$$

For hydrated proteins the conductivity increases logarithmically with adsorbed water content up to about 10% of adsorbed water and begins to level off at higher proportions of adsorbed water. Electrolysis experiments[432-434,441] indicate that the conduction is primarily electronic at low water contents (perhaps intrinsic but possibly via injected charge),[253,435] but is predominantly protonic at higher water contents. Cellulose,[436,437,454b] gelatin,[423b,438] collagen,[434,493] and melanin[434] behave in a similar fashion. The changeover from primarily electronic to primarily protonic conduction has been explained[439] for hemoglobin as arising when sufficient water is adsorbed to create a contiguous path of water molecules through which the protons may pass.[440] The results suggest, furthermore, that the fibrous protein collagen, and perhaps other proteins as well, may even be intrinsic proton conductors in the vacuum-dried condition.

Rather similar results to those for the proteins are observed for DNA, with predominantly electronic conductivity at low hydration, changing to a protonic conductivity at about the water content corresponding to the transition from the ordered, crystalline state to the disordered state.[441-443]

The possible biological significance of conduction in biosystems is of central interest (see ref 8b, 422, 423, 444, 445, 495). If the observed behavior arises from electrode or surface effects alone, and not from intrinsic properties, then this work can be regarded as being of a semitechnical nature without much importance in other connections.[429,435] On the other hand, it is suggested that, while proton conduction should not be regarded as a general process which can be freely invoked in the explanation of any biological phenomenon, there are certain phenomena (such as some enzymatic processes)[446,447] which require fast proton transfers over extended distances on a molecular scale, for which a cooperative

proton transfer system would seem to be required.

One biological system which deserves consideration here is the lipid membrane;[496] this is of particular interest because it can be modelled synthetically, as a bimolecular membrane, in a condition suitable for transport studies.[448,497] Net ion transport occurs across such membranes by various mechanisms involving either permanent or transient modifications of the basic structure. Together with this there is a small leakage conductance which is in general rather ill-defined.[449] Phospholipids, however, have an appreciable conductivity, and they exhibit a large activation energy at low temperatures and a smaller activation energy above a temperature associated with a transition from a crystalline (or more ordered) phase to a mesomorphic state, while electrolysis yields hydrogen gas.[434] These observations have been related to the fact that the phospholipids contain hydrogen-bonded polar regions, and a mechanism for conduction involving proton transfer and group rotation, as in the alcohols and polyamides, has been postulated.[450] The situation may, however, be somewhat more complex than here described, with different charge-carriers in different pH ranges.[451]

V. Summary and Conclusions

Table III lists those materials upon which experiments have been performed which show that ionic conduction can occur to yield hydrogen gas; the few in which emf experiments have been performed are also noted. This list should not be regarded as a list of certain proton conductors but rather as a group of likely contenders, because of the possibility of electrode reactions by which the conducting ion is discharged and hydrogen gas is produced in a subsequent process. The emf experiments provide better information in this respect, but are incomplete in not providing conductivity data. Bruinink[1] states that the only unambiguous experiment for demonstration of proton conduction is the electrolysis of a specimen between two protodes, with the condition that the amount of hydrogen consumed at the anode on passage of current is equal to the amount of hydrogen produced at the cathode. This experiment will only be a clear demonstration of the total ion transport number, however, and will not distinguish among different ion carriers because, again, of possible reactions at the electrode.[24] The experiment is thus supplemented, following Tubandt,[25] by utilizing a number of samples in series, passing current, and analyzing the samples for accumulation of material not reversible to the electrodes used, as described by Bruinink[145] on KHF_2. No fully satisfactory protode is known, but it is possible that known protonic conductors, such as imidazole[283] or $NH_4H_2PO_4$,[164] may be used for this purpose, as proton source and sink, on either side of the sample under study.

Surveying the materials discussed on the previous pages, it does seem likely on various grounds that many among them (and indeed among other similar compounds not yet studied) are proton conductors, and they will be so treated in the discussion which follows. It is immediately apparent that there are, at least, two classes of proton-conducting materials: (1) those in which no chain of hydrogen bonds exist, and in which proton conduction must be by interstitial motion; and (2) chain hydrogen-bonded substances, in which cooperative proton transfer processes may occur. These will be discussed briefly below.

(1) Interstitial Proton Conductors. The bare proton has, because of its uniquely small ionic radius, an exceptionally high charge density which may be expected to polar-

ize its surroundings quite considerably;[204] for this reason it is hardly conceivable that a bare proton could migrate independently through a crystal as does, for example, a silver ion through the silver iodide structure. Rather, the proton should be conceived as migrating from one site of temporary coordination to negative ion to another such site.[145] An example of this would occur in the migration of injected protons into $LiIO_3$, or of protons through a structure such as that of α-FeOOH, or during a thermal decomposition. In the case of KHF_2, where proton migration is isotropic and must be interstitial, it is supplemented by K^+ conduction when the transition to the β-phase occurs, a transition which introduces a considerable degree of disorder into the structure. In this respect, then, the proton is simply one among the variety of ions which can participate in conduction by interstitial migration.

(2) Chain Hydrogen-Bonded Proton Conductors. Interstitial proton conduction may also occur in chain hydrogen-bonded materials. More interesting, however, is the possibility of cooperative proton transfer processes which will usually reverse the orientation of the hydrogen-bond chain and require a rotational process to permit the reorientation which is required if a continuous current is to flow. It is striking that the conductivity of many such materials becomes demonstrably ionic (and probably protonic) only at higher temperatures, above a transition to a phase in which rotation can be expected, or in a disordered phase (in the paraelectric phase of ferroelectrics), or near to the melting point.[452] This observation may be at least partially conditioned by the lower conductivities which are inevitably found at lower temperatures since these conductivities obey an Arrhenius law. Other materials in which proton conductivity might well be expected, such as NH_4HCO_3 or the amino acids or oxalic acid dihydrate, do not have a corresponding phase transition, and there is generally no clear evidence of proton motion or group rotations.

A major consideration in the interest that has been displayed in cooperative proton transfer processes has been the possibility of exceptionally high mobilities along the chain. This possibility was occasioned by Eigen, de Maeyer, and Spatz's value[387] for the proton mobility in ice, derived from high-field current saturation experiments, of about 0.1 cm^2 V^{-1} sec^{-1}. This value is not much smaller than the value, 1 cm^2 V^{-1} sec^{-1}, found for semiconductors, and it was hoped that the proton transport could be described in quantum-mechanical terms, treating it as delocalized in an energy band. Successively improved measurements and the elimination of surface effects have, over the years, brought this value down to within the upper end of the range expected for a normal ion conductor. A very low mobility cannot be treated by band theory because of violation of the uncertainty principle;[453,454a] for protons the lower limit of a band mobility appears to be about 10^{-4} cm^2 V^{-1} sec^{-1}.

For other materials, rather low mobilities are generally calculated; the experimental data, however, are usually too unreliable to justify anything but a qualitative assessment. The general impression is that improved techniques yield lower mobilities. The results seem to suggest then that the hope of a very fast proton transfer process, associated with a high mobility, is probably vain. Nevertheless, the activation energies observed (perhaps 20 kcal mol^{-1}) are generally small compared with those obtained with other ionic conductors (about 50 kcal mol^{-1}, or greater)[10] so that, with efficient protodes, it may be possible to obtain relatively high proton currents. Such efficient, ohmic protodes will only be effective if the rate-determining step in the sequence is, indeed, the proton

TABLE III. Direct Indicators of Proton Conduction in Solids[a]

Material[b]	Solid phase[c]	Proton efficiency, %	Temp, °C	Method[d]
(1) Lacking Stoichiometric Hydrogen				
ThO_2	pp, with M^{3+}	100	>1200	Conductivity[92]
SiO_2	Vitreous	58	1000	H permeation in field[96]
SiO_2	Film		250	^{3}H injection[99]
H_xWO_3	Powder			Mobility by nmr[107]
$LiIO_3$	sc		Room	SCLC[110]
(3) Isolated Hydrogen Bonds				
KHF_2	pp, α-phase	100	<196	Electrolysis[143] Emf[145]
	pp, β-phase	~0	>196	Emf[145]
(4) Hydrogen Bond Chains, Broken by Intramolecular Links				
NH_4Cl	sc, with urea	0–60	<185	Emf[150]
	sc	100	Room	Electrolysis[164]
NH_4ClO_4	pp, sc	100	Room	Electrolysis[163,164]
		0	30–200	Comparison with $RbClO_4$[169,170]
TGS	...	...	...	Electrolysis[20]
KH_2PO_4	sc, with H_2SO_4	100	Room	Electrolysis[185]
$NH_4H_2PO_4$	sc	93	>Room	Electrolysis[201,202,436b]
$(COOH)_2 \cdot 2H_2O$	pp	100	Room	Electrolysis, but only under high fields[222,434]
$CuSO_4 \cdot 5H_2O$	sc		Room	SCLC, ^{3}H injection from satd aq soln[243]
Borax	pp	>60	>21	Electrolysis[239,247]
	pp	5–30[e]	From 15	Electrolysis[244]
Tincalconite	pp	5–35[e]	From 26	Electrolysis[244]
$K_{1.64}Pt(C_2O_4) \cdot xH_2O$				Cell[260]
	pp		Room	Redox[261]
Imidazole	pp	98	Room	Electrolysis[283]
	sc, ‖ c	90	31	Electrolysis[282]
	sc, ‖ a	28	31	Electrolysis[282]
Urea[h]	sc, ‖ c	70	Room	Electrolysis, with injection[283]
Uronium nitrate	pp	100	60	Electrolysis with mass transport[476]
(5) Linked Chains of Hydrogen Bonds				
$Li_2SO_4 \cdot H_2O$	pp	100	15	Electrolysis,[301] SCLC[305]
$LiN_2H_5SO_4$	sc, ‖ c	100	Room	Electrolysis[185,313]
Cetyl alcohol	Polycryst, α-phase	"Greater part"	40–50	Electrolysis[343]
Ice Ih	Polycryst	100[f]	~−10	Electrolysis,[382] mass transport,[383] emf[384]
	sc		−196	SCLC[385a]
(6) Polymeric Systems				
Polyamide	Nylon 66	~50	>120	Electrolysis[410]
		0	<100	Comparison with non-hydrogen-bonded polymer[409]
Polysulfinimide	Hydrated	100[e]	Room	Electrolysis[412]
Polyglycine	>3% hydrated	...[e]		^{3}H diffusion[g] in field[414]
(7) Biological Systems				
Cellulose	Dry	50–100[e]	~160	Electrolysis[416,437]
Melanin	Hydrated	65	Room	Electrolysis[434]
Keratin	Hydrated	90[e]	Room	Electrolysis[432]
Methemoglobin	>10% hydrated	<50[e]	Room	Electrolysis[433,434,441]
Cytochrome c	Hydrated	<90[e]	Room	Electrolysis[434]
Gelatin	Hydrated	...[e]		$\sigma_{D_2O}/\sigma_{H_2O}$[473]
Collagen	Dry	100[e]	Room	Electrolysis[434]
Lecithin (lipid)	Hydrated	<80[e]	Room	Electrolysis[434]
Na-DNA	>35% hydrated	<90[e]	Room	Electrolysis[441]

[a] Extended table, after Bruinink.[1] [b] Classification follows section III.A. [c] pp, pressed pellet; sc, single crystal; polycryst, polycrystalline sample. [d] Abbreviated description. SCLC = space-charge limited currents, but together with other relevant observations. [e] Subject to extent of hydration. [f] This may be an impurity or electrode effect,[377] [g] A Chemla-type experiment: M. Chemla, *Ann. Phys. (Paris)*, [13] **1**, 959 (1956); see also ref 5. [h] Also thiourea, benzimidazole, and succinimide.

injecting step; for some materials it may be that a molecular rotation or even a proton transfer is rate determining.[455]

It seems worthwhile to propose a tentative set of criteria for proton conduction, based upon experience, which may be helpful in guiding the experimenter's choice of a system worthy of investigation for its proton conductive ability, or the theorist's analysis of the favorable conditions for conduction, and, hopefully, in leading the synthetic chemist toward the construction of an effective proton conductor. The discovery of any such material will be of significance in fuel cell and other electrochemical technology,[498] and will inspire new interest in consideration of the biological implications of proton conduction.

The criteria proposed are:

(a) The protons should be involved in hydrogen bonds, for this weakens their covalent attachment to their electronegative neighbors and encourages proton transfers across the bonds.[394]

(b) There should be suitable paths for proton motion in the form of a network of hydrogen bonds along which transfer may occur; such a network may consist of directly linked hydrogen bonds, as in ice, or a sequence of such bonds broken by appropriate intramolecular links.

(c) The system of bonds should not be so rigid that the possibilities of molecular rotation are excessively limited.

It is clear that there is something of a conflict between criterion a, which demands a moderately strong hydrogen bond, and criterion c which requires that it be not too strong; in the words of Thomas, Evans, and Lewis,[127] "a delicate requirement of order . . . is demanded for contiguous molecules . . . (so that) special conditions need to be fulfilled to permit of protonic conductivity in the solid state." Eley,[456] too, has pointed out that too rigid a hydrogen-bonded framework, as in the β-protein structure, prevents chain rotation, and hence proton conduction; conversely, the smaller number of hydrogen bonds in polyamides is not so restricting, and proton conduction becomes possible. The same conclusion has been reached by Seanor[410] in respect to polyamides.

The phenomenon of proton conduction only after injection, in a material like urea, receives explanation in terms of these criteria in that such a solid lacks intrinsic, mobile protons (controlled, perhaps, by a low proton mobility across the hydrogen bond; cf. criterion a), but has the conducting paths which may be utilized by injected protons.

VI. Addendum

The following is added in an attempt to bring the coverage of this review up-to-date (if that is ever possible!) at the time of going to press, and covers literature which has appeared or become available in the period to Aug–Sept 1974. The material is divided into the same sections as make up the body of the review.

I. Some additional review literature has come to hand. Sorokin[503] has examined the effects of intramolecular interaction on the physicochemical properties of conductors with reference to the carboxylic acids. The coverage of the ferroelectric literature is much extended by the appearance of a new member of the series "Solid State Physics Literature Guides," edited by Connolly,[504] and by a chapter in a forthcoming review of hydrogen bonding.[505] From an analysis of the geometry of hydrogen bonds from donor water molecules in crystals, it appears

that the equilibrium configuration of the bond is linear, rather than nonlinear as earlier suggested,[13] and isotropic[506] (see also section III.A). Schmidt,[507a] basing his argument on the Einstein relation between conductivity and diffusivity, has suggested that intrinsic proton conductors will have values for σ_0 about 10^3 ohm^{-1}·cm^{-1}, doped materials will have smaller values, while cracked, polycrystalline and powdered materials will have anomalously large values for σ_0.

II. The problem of the formation of ohmic electrodes and of space charge formation continues to exercise the minds of both experimentalists and theoreticians. Montojo and Sanchez[508] have shown that passage of ion current (K$^+$) through a conductor (KBr) promotes the formation of a new electrode (K) which then acts as injector of electrons; obviously the later details will not coincide in a proton conductor, but the initial phases of formation of a stable contact deserve consideration in the light of this work. The internal space charge distribution in a crystal has been examined[509] by measuring photocurrents induced on shining weakly absorbed light through successive crystal layers parallel to the electrodes; this could be applied to proton conductors if suitable wavelengths for the incident light could be found. The space charge problem is avoided if a truly "ohmic" electrode can be formed; Auvert and Kahane[507b] have apparently succeeded in forming ohmic electrodes to an ice single crystal by using a low-temperature hydrogen plasma as the electrode. They find an ohmic conductivity at −10° of 2×10^{-8} ohm^{-1} cm^{-1}, with an activation energy of 6.6 kcal mol^{-1}.

The analysis of the electric polarization which occurs with the discharge of ions is presently under serious discussion; Mitoff and Charles[35,510] attempted to explain this in terms of a one-mobile charge-carrier approach, while Macdonald prefers the use of his generalized two-mobile charge-carrier theory.[46,511] Macdonald's work is of great importance but, as Mitoff and Charles[510] indicate, it may be very difficult to apply.

The conditions for fast ion conductivity in solids have been examined by van Gool;[512] for the β-aluminas it appears that high conductivity requires the presence of excess equivalent sites for the mobile ion. This may be appropriate in interstitial conduction in proton conductors, but will not affect discussion of cooperative proton motion through a chain of hydrogen bonds. Proton nmr studies[513] of LaNi$_{5.3}$H$_6$, previously suggested[26] as suitable for a protode, indicate that the hydrogen "atoms" are very mobile so that there probably exist a number of equivalent sites for each atom.

IV.A.1. In α-quartz, further evidence[514] confirms[97] the mobility of both alkali metal ions and protons (impurity) along channels in the structure, perpendicular to the optic axis. The phenomenon of hydrogen "spill over,"[107,108] by which H$_x$WO$_3$ is prepared from WO$_3$ in a hydrogen atmosphere, has now been fully reviewed;[515] apparently, hydrogen dissociates on a metal and then migrates to acceptor sites.

IV.B.1. A practical aspect of the low conductivity of dry granulated sugar, the danger of static build-up during processing, is discussed by Krutikova and Kostenyuk,[516] who note the rapid increase in conductivity with water content. Bruinink[517] has continued his study of the KHF$_2$ system and, on the basis of ac polarization effects, has confirmed the earlier assignment[144,145] of the low temperature α phase as a proton conductor; the high-temperature β phase shows pronounced polarization effects in hydrogen atmospheres, indicative of the different conduction mechanism which is in operation.

IV.B.2. The problem of preparing pure ammonium halide single crystals appears to have been solved by vapor-phase growth; pure NH_4Cl is reported to have a high-temperature dc activation energy of 30 kcal mol^{-1} and a low-temperature dc activation energy of 19 kcal mol^{-1}, while the corresponding values for NH_4Br are 25 and 16 kcal mol^{-1}, respectively.[518] Other reports on conduction in NH_4Cl have also appeared.[519,520] Ammonium sulfate decomposes on heating to NH_4HSO_4, which acts as a proton donor;[521] HSO_4^- also acts as a donor to KDP,[188] to ADP,[522] and to NH_4ClO_4.[523] The latter compound can take up NH_3; the complex $NH_4ClO_4 \cdot 2NH_3$ has an ac conductivity which is 10^{12} times larger than that of NH_4ClO_4—the conductivity is believed to be protonic.[524]

The crystal structures of ADP and ADA have recently been refined,[525] while examination of the high-temperature phase transitions in KDP continues.[526] A comprehensive summary of the phase behavior in the KDP family is to be published by Pistorius.[527] Further conduction studies on KDP,[528] ADP and HSO_4^--doped ADP,[529] and KDA and deuterated KDA[530] yield results similar to those reported in the main body of this review.

The crystal structures of $KHCO_3$ and of $KDCO_3$ at 298, 219 and 95 K have been redetermined,[531] and it appears that there is some 15–20% of statistical disordering in the orientation of the HCO_3^- and DCO_3^- ions.

Further evidence for proton transfer across a hydrogen bond in an irradiated amino acid crystal, L-cysteic acid monohydrate, has appeared.[532] There is no indication, however, of larger scale translations of protons. A brief mention of the dielectric properties of hydrates appears in a recent book by Hasted.[533]

Bruinink (personal communication) has noted that Kawada, et al.,[282] found 10^5-fold greater conductivities for imidazole during electrolysis experiments than in their conduction experiments, which he ascribes to a large surface conduction contribution. In addition to the high solid-state conductivities already noted for N,N-diphenylacetamide,[293] an appreciable conductivity has been noted for N-methylacetamide.[534]

IV.B.3. Schmidt and Parker[535] have shown that the apparent ferroelectric hysteresis loops observed for lithium hydrazinium sulfate (which is not ferroelectric) arise from the partially blocked protonic conductivity in the crystal.[308] For FeOOH, Kaneko and Inouye[536] assume the carriers to be excess d electrons rather than protons since the sign of the Seebeck coefficient indicates negative charge carriers (in the α- and γ-phases, at least). Addition of water (up to 3%) to cetyl alcohol increases its conductivity sevenfold;[537] deuteron magnetic resonance indicates that the water is in a solid-like form, and a Grotthus conduction mechanism is proposed for the system.

Interesting conductivity studies on cupric formate tetrahydrate single crystals are reported by Weber and Flanagan;[538] using saturated solutions of this salt for protodes, space-charge controlled currents were observed with a tenfold better conductivity parallel to the water planes than perpendicular thereto, while the perpendicular conductivity rises to the parallel value at high humidities (70% relative humidity, with the crystal stable down to 50%). An interesting feature of the results is that this anisotropy disappears if cleaved crystals are used, suggesting that damage has occurred in such crystals.

Discussion on the electrical properties of ice continues at an intensive pace. Hasted has reviewed the dielectric properties,[533] von Hippel has marvelously summarized[539] the recent work of his M.I.T. group and of others in a survey of the molecular processes in the phases of water, and Shemelin provides a general review of electrical and mechanical properties of ice.[540] Glen's remarks[507c] on the present understanding of conduction properties in ice should be noted. Sokoloff, by a method similar to that used by Minagawa,[458,541] has shown[542] that no Hall effect can be expected in ice if defect transport is by tunnelling while, in the case of thermally activated transport, the Hall effect must fall to zero at low temperatures. Ham and Rose confirm[543] a very low Hall effect in HF-doped ice (a Hall coefficient for positive carriers of $4.2 \pm 2.8 \times 10^{-3}$ cm^2 V^{-1} sec^{-1} at $-5°$); this difference from earlier values[385b] may be due to a high dislocation density in the doped ice,[507d,544] but indications[543] seem against the earlier, higher Hall coefficient.

Various theoretical studies on ice have appeared, hampered by the experimental uncertainties. Onsager and colleagues,[545] using a model similar to that of Minagawa,[458] have studied the hopping of ions in ice, while Hofacker and colleagues[546] have considered the role of proton–proton interactions in the proton-transfer processes. Nagle has calculated[547] the dielectric constant of ice, and Hubmann has applied[548] experimental results on ice to Jaccard's defect theory (cf. ref 359a) of the electrical properties of ice.

IV.C. Uemura[549] has developed a simple theory for the ionic contribution to the dielectric constant and loss in a polymer, and Miyamoto and Shibayama[550] have devised a generalized ion conduction theory. Two studies[551,552] report on the conductivity of nylon 66; Isoda, et al.,[552] believe that the ion carriers derive from impurities rather than amide protons. The electrical properties of celluloid have also been examined.[553]

IV.D. von Hippel, et al.,[554] have discussed the place of protons in the dielectric analysis of biomaterials. The conductivity of nucleic acids has been discussed with respect to electronic contributions,[555-557] and to ionic contributions and the effect of hydration.[558-560] Interest in proton transfer through membranes is of continuing interest,[561-566] but the molecular details of the process remain in considerable doubt.

V. The experimental evidence accumulating seems to confirm that "proton semiconduction," as a quantum phenomenon, is not found (even in ice). However, facilitated proton transport along a hydrogen bond chain remains a concept worthy of detailed study.

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