Structure and Properties of Ice[1]

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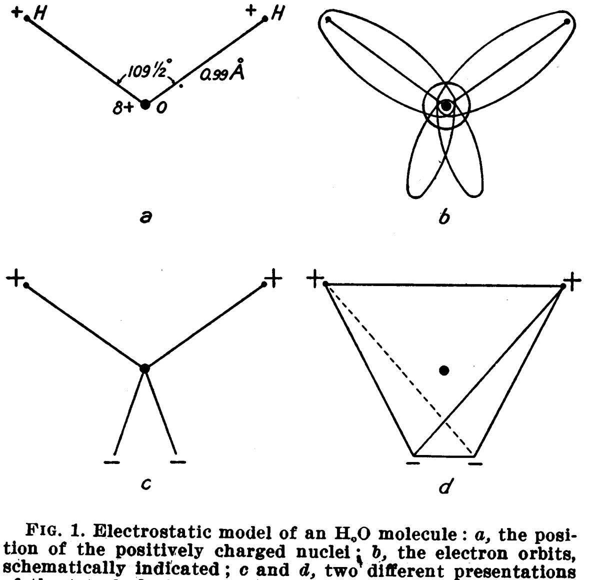
WATER is not only one of the most common and most important chemical compounds, but it is also one of the most anomalous and intriguing. Its problems have been treated in innumerable papers. To reach a full understanding of its behavior, we must first elucidate the properties of ice. This problem is easier because the structure of ice is simpler and better known than that of water. I have tried to deduce the properties of ice from a simple electrostatic model of the H_2O molecule, and I shall review the results obtained.

A tetrahedral model of the H_2O molecule. We know from Mecke (*1*) that the three nuclei of an H_2O molecule form an isosceles triangle with the oxygen nucleus at the apex and the two protons on the base line. The sides are (in water vapor) 0.97 A, and the apical angle 106°; hence, they are nearly equal to the tetrahedral angle 109.5°. In ice the sides are *ca* 0.99 A (*2*), and we shall assume that the apical angle is exactly the tetrahedral one (Fig. 1, *a*). The three positive nuclei are encircled by ten electrons. Two of them circle quite close to the oxygen nucleus, and the eight remaining electrons circle in pairs in four eccentric orbits, which radiate tetrahedrally from the oxygen nucleus, and of which two include the two protons (Fig. 1, *b*). The electron orbits completely screen the positive charge of the oxygen nucleus. They also screen a considerable part of the charge of the protons but give an excess of negative charge in the direction of the two orbits that do not contain protons. As model of an ice molecule we shall therefore use a regular tetrahedron of radius 0.99 A, with positive charges on the two corners and negative charges on the other two (Fig. 1, *c* and *d*). In order to give the tetrahedral model the known dipole moment of the H_2O molecule (1.87 Debye), the electrical charges on the corners must be $\pm 0.171\ e$ (e = the electronic charge). In ice these tetrahedra are placed at a mutual distance of 2.76 A. We shall therefore imagine an ice molecule as a sphere of diameter 2.76 A, inside which four electric charges are placed in a regular tetrahedral arrangement.



a *b* *c* *d*

FIG. 1. Electrostatic model of an H_2O molecule: *a*, the position of the positively charged nuclei; *b*, the electron orbits, schematically indicated; *c* and *d*, two different presentations of the tetrahedral model of the H_2O molecule.

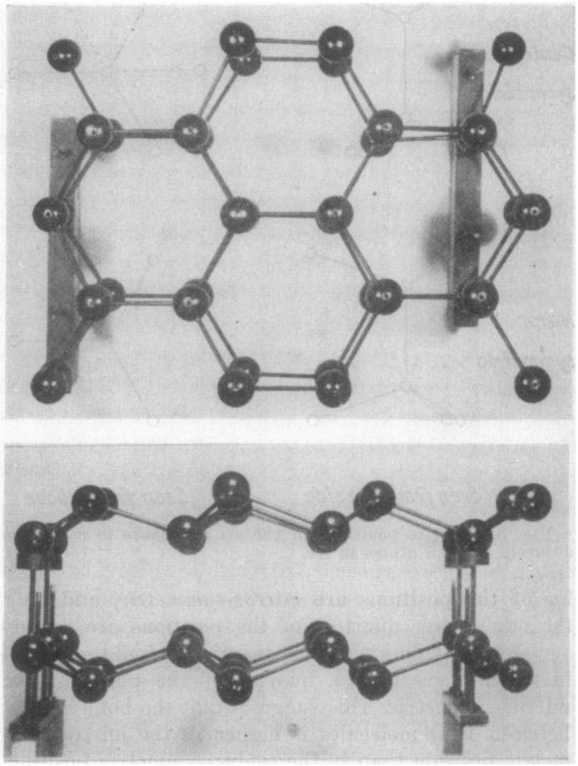


FIG. 2. Model of an ice crystal, reproduced from W. H. Bragg, *Proc. Roy. Inst. Gt. Brit.*, **30**, 283 (1938).

The crystal structure of ice. In an ice crystal the molecules—or more exactly, the oxygen atoms—lie in puckered hexagonal layers, in which the oxygen atoms are raised and lowered alternately (Fig. 2). Adjacent layers are mirror images, and the sizes of the parameters are such that each atom is surrounded by four oxygen atoms in regular tetrahedral arrangement at a distance of 2.76 A (Barnes [*3*]). The regular tetrahedral arrangement is a consequence of the tetra-

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[1] Based on a paper published in *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **27**, (1), (1951).

hedral structure of the H_2O molecule. Each positive corner of a molecule is attached by electrostatic forces to a negative corner of another molecule and forms with it what is often called a hydrogen bond.

A substance in which every atom has four neighbors in regular tetrahedral arrangement can crystallize hexagonally (as ice) or cubically (as diamond). Let us try to find out why ice crystallizes hexagonally and not cubically. The difference between the two structures lies in the arrangement of the six neighbors around a pair of adjacent atoms. In the cubic diamond crystal, the position is always *center-symmetric* (Fig. 3), whereas in the hexagonal ice a quarter of the positions are *mirror-symmetric,* and only the other three quarters of the positions are center-symmetric. It does not seem possible to build a crystal in which more than a quarter of the positions are mirror-symmetric. This suggests that the bond energy between H_2O molecules is higher in the mirror-symmetric position than in the center-symmetric position. The suggestion is supported by some old and accurate x-ray measurements on ice by H. D. Megaw (*4*). From these measurements I have calculated that the mirror-symmetric bonds in ice are *ca* 0.5 per cent shorter than the center-symmetric ones, a not insignificant difference, considering the low compressibility of ice. This suggestion is even more directly supported by the following calculation: Using for the H_2O molecule the electrical model described above, the electrostatic lattice energy can be calculated, for a hypothetical cubic ice crystal with all bonds center-symmetric, to 14.51 kcal/gmol, and for the ordinary hexagonal ice crystal, with a quarter of the bonds mirror-symmetric, to 14.93 kcal/gmol—i.e., 0.42 kcal/gmol higher. The calculated values are valid at low temperatures. For reasons that are given below, the values decrease somewhat with increasing temperature and approach each other slightly at the melting point.

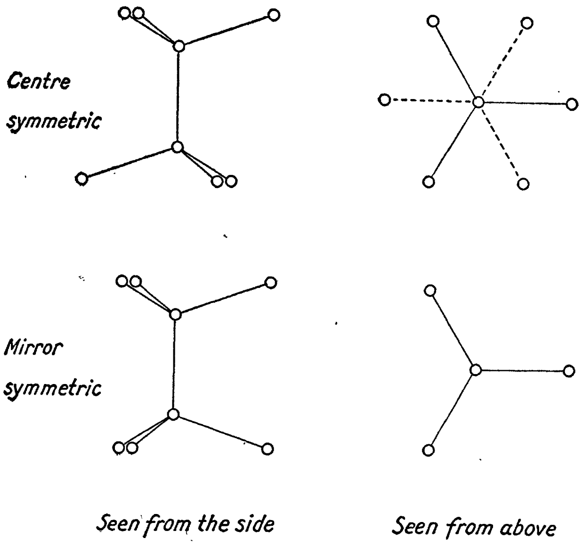

FIG. 3. The two positions of the six neighbors to a pair of adjacent oxygen atoms in ice.

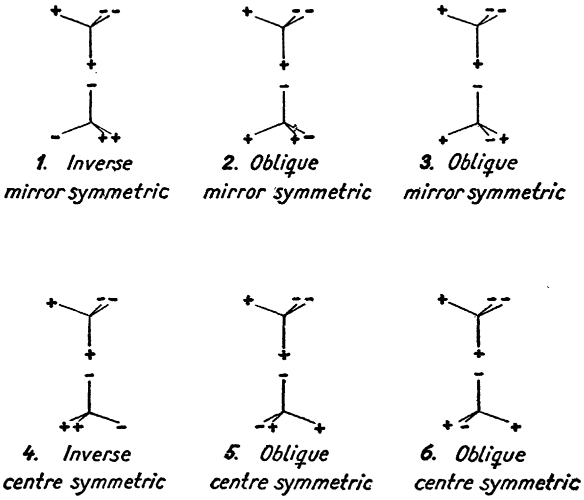

FIG. 4. The six positions of two neighbor molecules in ice.

The configurations of an ice crystal. As yet we have only considered the arrangement of the *oxygen* atoms in ice. The arrangement of the *protons* is a much more complicated question. We have good reason to believe the H_2O molecules are arranged in such a way that the protons always lie on the lines connecting adjacent oxygen atoms, and that there is one, and only one, proton on each of these lines, forming with the two oxygen atoms what is often called a hydrogen bond. There exists a very large number of configurations fulfilling these conditions. The reason is that both the center-symmetric and the mirror-symmetric bonds can be either inverse or oblique (Fig. 4). Pauling (*5*) has calculated this number of configurations of an ice crystal to 1.5^N, where N is the number of molecules in the crystal. This is a very large number, even in comparison with astronomical figures. For 18 g of ice it is a number with more than 10^{23} figures. Pauling is of the opinion that all configurations have nearly the same lattice energy and are therefore equally probable even at low temperatures. If, however, we accept the tetrahedral model described above, the electrostatic bond energy is considerably higher

TABLE 1

ELECTROSTATIC BOND ENERGIES BETWEEN ADJACENT MOLECULES IN ICE IN 10^{-12} ERG

	Without correction	Corrected for second neighbors' attractions	
		Low temp	High temp
Inverse mirror-symmetric	0.5067	0.5196	0.5395
Oblique " "	.4319	.4781	.4713
Oblique center-symmetric	.4792	.5143	.5143
Inverse " "	0.4117	0.4532	0.4547

for the inverse mirror-symmetric positions than for the corresponding two oblique mirror-symmetric positions, and the energy for the two oblique center-symmetric positions is higher than for the corresponding inverse center-symmetric positions (Table 1).

The number of the two bond types with high bond energies must increase with decreasing temperature at the cost of the two other types. This makes a correction for the electrostatic energies between every other molecule very complicated. In Table 1 corrected values are given corresponding to low temperature, where only the bonds with high bond energy are present, and to high temperature, where all the bonds present are in the statistically expected amount. By means of a Boltzmann equation approximate values are calculated for the ratio between inverse and oblique positions at several temperatures (Table 2).

TABLE 2

APPROXIMATE PERCENTAGES OF INVERSE AND OBLIQUE POSITIONS IN ICE

	273° K	136.5° K	90° K	68.25° K	Statistical percentage
Inverse mirror-symmetric	68.4	90.4	97.7	99.44	33.3
Oblique mirror-symmetric	31.6	9.6	2.3	0.56	66.7
Oblique center-symmetric	90.9	98.0	99.62	99.92	66.7
Inverse center-symmetric	9.1	2.0	0.38	0.08	33.3

Application of the Boltzmann equation is not fully justified, and calculated values therefore must be used with caution. Even at the melting point the percentages are far from being the statistical ones, corresponding to equal energies.

Heat of sublimation. By means of the figures in Table 2, the electrostatic lattice energy of an ice crystal can be calculated. Since the ratio between inverse and oblique positions changes with temperature, the lattice energy will be dependent on temperature. At low temperatures, when only inverse mirror-symmetric and oblique center-symmetric positions are present, a value of 14.93 kcal/gmol is found; and at high temperatures, when the ratio between inverse and oblique positions is as 1 to 2, a value of 14.32 kcal/gmol is found.

The electrostatic lattice energy constitutes the main part of the heat of sublimation of ice (12.14 kcal/gmol). In order to calculate more accurately the heat of sublimation, it is necessary to subtract the potential of the repulsive forces that hold the molecules in place at a distance of 2.76 A and to add the potential of the van der Waals' forces. By means of a triangular-model for the H_2O molecule, Bernal and Fowler (*6*) have calculated a heat of sublimation of the right order of magnitude. Using their estimated corrections for the repulsive forces (-6.8) and for the van der Waals' attraction ($+4.1$), we calculate for the heat of sublimation:

At low temperature $14.93 - 6.8 + 4.1 = 12.23$
At high temperature $14.32 - 6.8 + 4.1 = 11.62$

which is in good agreement with the observed value of the heat of sublimation 12.14 at 0° C and corrected to 0° K 11.81.

Zero-point entropy. From the behavior of ice in an alternating electric field we know that, at the melting point, the configuration of the ice changes rapidly, but that, at the temperature of liquid air (*ca* 90° K), the configuration freezes in. At this temperature, according to Table 2, about 99 per cent of the positions are the most stable ones. This explains why the heat capacity irregularities in the temperature range where the configuration freezes in, as found by Giauque (*7*), are small. The irregularities are so small that they seem to indicate that at 90° K only 0.1 per cent of the positions with small bond energies are present.

Pauling (*5*) is of the opinion that all the 1.5^N configurations of an ice crystal are equally probable even at the temperature where the configuration freezes in, and by means of this assumption he calculates the zero-point entropy of ice to $R \ln 1.5 = 0.806$ kcal/gmol/degree, in good agreement with the observed value 0.82 ± 0.15. If the configurations are not all equally probable at the temperature where they freeze in, then the observed zero-point entropy should be smaller than Pauling's value. The figures in Table 2 for 90° K suggest a value of only a few hundredths of Pauling's value; consequently it seems necessary to find another explanation of the observed zero-point entropy.

Changes in configuration and molecular turns. Debye (*8*) has explained the high dielectric constant of ice (*ca* 80) by the existence in ice of electric dipoles, which frequently turn from one position of equilibrium to another under the influence of the thermal movements. From the behavior of ice in an alternating field, Dorsey (*9*) has calculated the rate of dipole turns per molecule to 0.83×10^6 sec^{-1} at 0° C, and from the temperature coefficients of dielectric properties the activation energy (the critical threshold energy) has been calculated to be from 9.3 to 14.6 kcal/gmol by a series of different authors. A value of 13 seems to be most probable.

It is difficult to explain the molecular nature of the frequent dipole turns in ice. The H_2O molecule is, of course, a strong dipole, and every molecule in the crystal lattice of ice can have its dipole axis in six different directions, all perpendicular or antiparallel to each other; but in an ideal ice crystal a single molecule (apart from the few surface molecules) cannot turn to another position of equilibrium. Only by simultaneous turning of all the molecules in a closed ring or in a row of molecules, beginning and ending in the surface, is it possible to change the configuration to a new equilibrium position. Such turnings, however, must be very improbable and, what is more important, by turning of all the molecules of a ring, the dipole moment of the crystal will not be changed, and these turnings therefore cannot be used for the Debye theory.

In every ice crystal, however, lattice faults occur, and at the fault sites it is to be expected that single molecules can easily turn to new positions and thus change the direction of their dipole axes. We must here direct our attention to such lattice faults as are caused by thermal movements, which occur in a concentration, determined by the temperature. There are two types of such faults: *orientation fault sites,* where two neighboring molecules are incorrectly orientated toward each other with two protons or with no protons on the line between their oxygen atoms; and *ionization fault sites,* where H_3O^+ or HO^- ions occur in the lattice instead of H_2O molecules.

Orientation fault sites. If, on account of strong thermal movements, an ice molecule has rotated at such a large angle that two protons happen to be placed between two oxygen atoms and no proton between two other oxygen atoms (Fig. 5 *b*), the chance that it will turn back is great, but it may happen that one of the adjacent molecules has turned before it turns back. In that case the site with two protons and that with no proton have been separated (Fig. 5 *c*). Continued molecular turns may cause the appearance of two independent fault sites of opposite types: sites with two protons, and sites with no proton between two oxygen atoms. These fault sites will migrate around in the crystal until they meet a fault site of the opposite type with which they can recombine. Under the influence of formation and recombination of the fault sites an equilibrium must be reached with well-defined and equal concentrations of the two types.

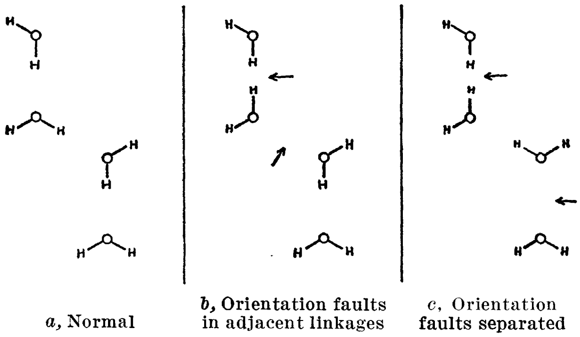
a, Normal — *b,* Orientation faults in adjacent linkages — *c,* Orientation faults separated

FIG. 5. Formation of orientation fault sites.

Two molecules between which there is an orientation fault site can easily turn to a new position, and every time one of the two molecules turns, the fault site is moved to a new position and the dipole moment of the molecule is rotated through 90°. The fault sites thus act as a kind of catalyst for the promotion of dipole turns.

If the previously described tetrahedral model is used, the formation of an orientation fault site can be estimated to require an energy $E_1 = 11.9 \pm 1.7$ kcal/gmol, and the activation energy for turns of molecules at a fault site can be estimated to be $E_2 = 2.5$ kcal/gmol. The energy of activation, corresponding to the temperature coefficient of the rate of molecular turns at orientation fault sites, is $E_1 + E_2 = 14.4 \pm 1.7$. The activation energy for the dipole turns which bring about the dielectric properties of ice was stated above to be *ca* 13. This shows that it is permissible to consider the molecular turns, occurring at the orientation fault sites as the dipole turns, as required by Debye's theory.

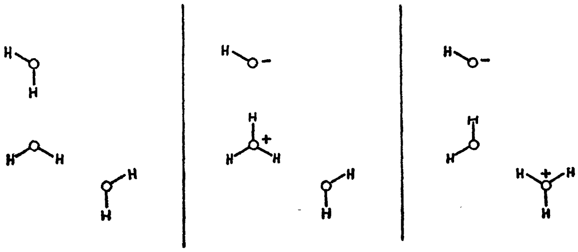
Normal — Ions in neighboring position — Separated ions

FIG. 6. Formation of ions.

It is not possible to calculate exactly the concentrations of the orientation fault sites in ice; but from certain reasonable assumptions I have estimated the concentration of each type to be one fault site for every 10^6 ice molecules, corresponding to a rate of molecular turns at an orientation fault site of *ca* 10^{12} sec^{-1}.

Ionization of ice. Ice has an electrolytic conductivity of a magnitude similar to that of water. Johnstone (*10*) gives the following values for the static (direct-current) conductivity of ice (κ):

Temp	0°	−1°	−4°	−10°	−19°
$\kappa \cdot 10^8$	(0.4)	(2.8)	0.23	0.11	0.026

The value at −1° is probably too high, on account of the impurities in the ice. The value given for 0° is extrapolated from the values at −4°, −10°, and −19°.

The conductivity of ice must be due to H_3O^+ and HO^- ions and their migration by means of proton jumps. It is improbable that these ions as units can migrate through the crystal lattice at rates that are of significance in this connection, or that other ions can do it. The H_3O^+ and HO^- ions are formed by proton jumps between two adjacent molecules: $H_2O + H_2O \rightarrow HO^- + H_3O^+$; and they are separated by means of proton jumps between the ions and H_2O molecules: $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$ and $HO^- + H_2O \rightarrow H_2O + HO^-$ (Fig. 6). The ions migrate in the ice by means of proton jumps until oppositely charged ions meet and have the opportunity of recombining.

The proton jump conductivities (μ) of H_3O^+ and HO^- ions in *water,* calculated as the surplus conductivities of these ions, compared with normal ions, are 200 and 105 at 0° C. The proton jump conductivities of these ions in *ice* must be assumed to be somewhat higher. In ice adjacent molecules are nearly always in the right position (hydrogen bond position) for proton jumps, but in water this is not the case. Correcting for this difference, I have estimated the molecular conductivities of the ions in ice to be 215 and 83 at 0°. From these conductivities and from the specific conductivity of ice, it follows that at 0° C 0.27×10^{-9} parts of the molecules are transformed to H_3O^+ ions and an equal amount to HO^- ions (in water 0.63×10^{-9} parts).

The failure of proton jumps in ice to explain the high dielectric constant. The rate of proton jumps in ice can be estimated from its conductivity. This can be done by means of an old formula of Einstein's (*11*), which connects the diffusion coefficient of a particle (the conductivity of an ion) with the mean displacement of the particle (the ion) in a given time. The rate is found to be 152 sec^{-1}/H_2O molecule at 0° C. This rate is *ca* 10^4 times less than the rate of molecular turns at orientation fault sites.

Proton jumps in ice are connected with dipole turns in a way similar to that in which migrations of orientation fault sites are. It has been proposed by several workers (*12–14*) that the dipole turns necessary for Debye's theory of the dielectric properties of ice may be the result of proton jumps and may be connected with the formation or the migration of H_3O^+ and HO^- ions. I myself have independently worked with the same idea. This idea, however, must be abandoned. The molecular turns produced by formation or migration of the ions are far too infrequent for this purposes (152 against 10^6), and, what is even more decisive, the molecular turns connected with the migration of the ions under the influence of an electric force produce a dipole moment in the direction opposite to that of the electric force and thus in the opposite direction to that required by Debye's theory. This can be seen in the following way:

The dipole moment produced by migration of the ions in an isolated block of ice is the vector sum of all the dipole moments, corresponding to the proton jumps connected with the ionic migration, each of which is 0.78 A. This dipole moment (P_1) can also be calculated as the sum of two dipole moments: the dipole moment P_2, produced by the ionic displacements, and the dipole moment P_3, produced by the molecular turns connected with the migration of the ions:

$$P_1 = P_2 + P_3. \tag{1}$$

The dipole moment P_2 is the vector sum of all the dipole moments produced by the individual ionic displacements. Each of these ionic displacements is parallel to a corresponding proton jump, but 2.76/0.78 larger. We must therefore have:

$$P_2 = P_1 \times 2.76/0.78. \tag{2}$$

From (1) and (2) follows:

$$P_3 = -P_1 \times 1.98/0.78.$$

It means that the dipole moment due to all the molecular turns connected with the migration of the ions is in the opposite direction of that corresponding to the proton jumps and numerically 1.98/0.78 times larger. Hence the molecular turns at the ions cannot explain the dielectric properties of ice. It is only the molecular turns at orientation fault sites which are responsible for these properties.

The proton jump conductivity of H_3O^+ and HO^- ions. The transport of electricity, corresponding to the movement of the H_3O^+ and HO^- ions in an electric field, is counteracted by the turns of dipole molecules connected with the movements of the ions. The transport would have been seriously hampered if the dipole moment produced by these turns were not incessantly cancelled by the molecular turns at orientation fault sites with a relaxation time of *ca* 10^{-6} sec (at 0°). To justify considering the conductivity of ice as a simple result of proton jumps, as is done in this paper, it is of decisive importance that molecular turns at orientation fault sites are *ca* 10^4 times as frequent as molecular turns at the ions.

In water the rate of molecular turns per ion must be similar to that in ice (*ca* 10^{12} sec^{-1} at 0°), and the rate of molecular turns per H_2O molecule, as calculated from the dielectric properties, is also *ca* 10^{12} sec^{-1}. Thus, even in the neighborhood of the migrating ion, the dipole moment produced by the migrating ion very quickly disappears. The old, but often criticized, explanation of the abnormally high conductivity of the H_3O^+ and HO^- ions in water, as due to migration of these ions by proton jumps, is thus fully justified.

The plasticity of ice. Ice is a plastic substance. This was first observed in the study of glaciers. The plasticity is due to the ease with which ice crystals glide along a plane perpendicular to the optical axis—that is, along the puckered hexagonal layers of which the crystal is built (Fig. 1). When a bar of ice, cut with its optical axis parallel to its length, is supported horizontally on two blocks, and when the portion between the blocks is loaded uniformly by means of a stirrup with a weight, then the portion directly under the load is slowly (in the course of hours) forced downward without creating optical discontinuities or changes in the optical properties of the ice (*15*). As the number of bonds between the puckered hexagonal layers is small, and as the bonds are all perpendicular to the layer, it is comprehensible that it is along this plane that the gliding takes place.

If all the molecules on one side of the gliding plane had positive (proton-containing) corners toward the plane, and all the molecules on the other side negative (proton-free) corners toward it, then the gliding could be easily understood. The molecules, however, turn at random positive and negative corners toward the gliding plane. If that were not the case, the ice crystal would be an extremely strong dipole. The gliding, therefore, must be combined with turns of the molecules. Consequently it is to be expected that the rate of gliding is connected with the rate of molecular turns in ice. This explains why the gliding rate decreases rapidly as temperature is lowered.

To produce gliding, a certain shearing force per cm^2 gliding area is necessary. This force seems to be about 5 kg/cm^2. When the force is increased above this minimum value, it is to be expected that the gliding rate in the beginning will increase strongly with the shearing force; but long before the rate approaches a critical value of 5×10^{-2} cm/sec, it is to be expected that the rate of gliding will increase only slowly with the force. At the critical rate the gliding distance, in the time a molecule makes a turn (10^{-6} sec), is equal to the distance between the molecules in the gliding plane (4.5 A). The existing observations seem to be in agreement with this conclusion, but they are not sufficiently accurate to verify it.

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News and Notes

Scientists in the News

Wm. A. Amberson, of the University of Maryland, will spend the months of August, September, and October as a guest professor in physiology on the medical faculty of the University of Vienna, lecturing on neuromuscular physiology.

Charles W. J. Armstrong, formerly head of the Chemotherapy Section, Laboratory of Hygiene, Department of National Health and Welfare, Ottawa, Canada, has been made director of the Division of Pharmacology, E. R. Squibb & Sons.

Harold W. Brown, director of the School of Public Health of Columbia University, has been appointed dean of the University of Puerto Rico College of Medicine, succeeding **Donald S. Martin,** who resigned. Dr. Brown was Chancellor Benitez' official adviser in planning the establishment of the medical college two years ago. An expert on tropical diseases, he had previously been a professor of parasitology at Columbia.

George F. Carrier, of Brown University, has been appointed Gordon McKay professor of mechanical engineering at Harvard. His work will be mainly in applied mechanics.

Recent visitors at the National Bureau of Standards included **John Cockroft,** director of the British Atomic Energy Research Establishment at Harwell; **Minoru Imoto,** of Osaka City University, Japan; and **E. C. Stathis,** professor of chemistry at the University of Athens. Dr. Stathis has been in the U. S. since last September, when he attended the Chemical Conclave in New York. He spent some time at the University of Minnesota with I. M. Kolthoff and has visited MIT and Harvard. He expected to leave at the end of March for England.

Robert Cruickshank, professor of bacteriology in the University of London at St. Mary's Hospital Medical School, is visiting 16 American and Canadian medical centers, among them the Communicable Disease Center, USPHS, at Alanta, and the laboratories at Chamblee. Dr. Cruickshank was guest of honor at a dinner sponsored by the CDC Branch of the Scientific Research Society of America at Emory University.

The California Texas Oil Company, Ltd., has announced the election of **George M. Cunningham** as president and **J. P. McCulloch** as vice president, of American Overseas Petroleum, Ltd., affiliate of Caltex engaged in exploration.

Richard A. Deno, chairman of the Department of Biological Sciences at Rutgers University College of Pharmacy, will join the faculty of the University of Michigan this fall as professor of pharmacognosy. He will teach two new courses in academic pharmacy.

Chauncey D. Leake, of the University of Texas Medical Branch, Galveston, has been given leave of absence to work on old Egyptian medical papyri at the Institute for Advanced Study. He is giving a series of talks at Eastern institutions on this subject this month and will speak at the Army Medical Library, Washington, Apr. 15, on "Leonardo da Vinci: Scientist and Artist."

Daniel Ludwig, professor of physiology at New York University, has resigned his post to accept appointment as professor of physiology at Fordham University.

Joy B. Phillips, of Morristown, N. J., has been appointed an instructor in zoology at Drew University and will join the college of liberal arts faculty in September. She has been a teaching fellow at Wash-