Proton Jumps and the Electrical Behavior of Ice and IceNH4F Solutions

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Proton Jumps and the Electrical Behavior of Ice and Ice-NH₄F Solutions*

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Previous suggestions that dielectric relaxation in ice may occur by means of proton shifts have been refuted by Bjerrum. Yet, the role of ions in this relaxation process cannot be ignored in view of the more recent studies on ice-NH₄F solutions, which indicate that solute ions can accelerate the rotation of ice molecules at a distance of 30 A or more from any ion.

Simple electrostatic calculations show that proton jumps in ice would entail the formation of "Bjerrum fault sites." In the case of pure ice, this might explain why: (a) the proton jump conductivity is much lower than in water at 0°C; and (b) the concentration of fault sites seems to be rather high, according to Bjerrum. Estimates of the frequencies of proton jumps and of activation energies show no disagreement of the proposed explanations with known facts.

In the case of ice-NH₄F solutions, proton jumps occurring between second-neighbor ion pairs, $F^- - H_2O - NH_4^+$, may also induce fault sites at the neighboring molecules. This ion-pair mechanism would agree with the low activation energy for these rates and with the peculiar concentration dependence of the frequency factor.

Finally, the thickness of the ion atmosphere should, at equilibrium, be less in ice-NH₄F solutions than in aqueous solutions of the same concentration. This, together with the above, might account for the changes with time in the dielectric relaxation rates of concentrated ice-NH₄F solutions observed immediately after freezing.
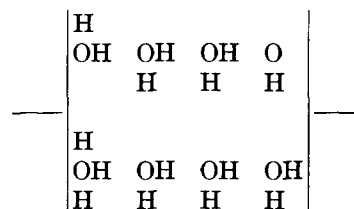
I. INTRODUCTION

ALTHOUGH the dielectric properties of ice have been thoroughly determined,[1] the mechanism of dielectric relaxation (or dipole rotation) in ice is still poorly understood. Of the numerous explanations proposed to date, that of Bjerrum[2] appears the most satisfactory. It assumes the presence of two or no hydrogen atoms along lines joining some adjacent oxygens; these can be called positive and negative "Bjerrum fault sites," respectively. Bjerrum estimates energies of about 10.5 kcal/mole for the existence of a fault site and of about 2.5 kcal/mole for the rotation of a molecule at a fault site, which would account for the observed activation energy of 13 kcal/mole for dipole rotation in ice.† He also rejects the idea that proton jumps might account for the observed dipole turns because of the following arguments: (a) At 0°C, one can estimate from conductivity measurements that the rate of proton jumps could be no more than 150 molecule⁻¹ sec⁻¹, whereas the observed number of dipole turns is between 4×10^4 and 10^6 molecule⁻¹ sec⁻¹. (b) Figure 1 shows that the polarization which results from proton jumps would be in the wrong direction. The orientation of the un-ionized molecules would be with the positively charged hydrogens toward the positive electrode, if proton jumps were the only cause of orientation changes.
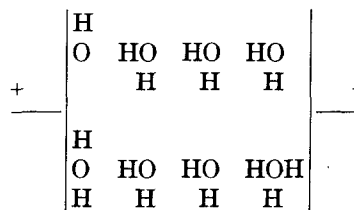
In spite of these powerful arguments, the part of ions in the relaxation process cannot be readily dismissed, in view of the more recent studies on ice-NH₄F solutions.[3,4] These indicate that the presence of about 0.1 mole/l NH₄F can cause a several hundred-fold increase in the rate of dipole rotation, and even for concentrations as low as 0.002-weight percent NH₄F, the rate at −35°C is several times faster than in pure ice. This can be shown to mean that, on the average, an ion can facilitate the rotation of molecules situated at a distance of as much as 30 A or more.[5] One might be tempted to attribute these effects to distortions produced by the ions in the ice lattice. However, such *marked distortions appear incompatible with the fact that NH₄F dissolves in ice in appreciable concentrations.*[3,4,6]

A more likely explanation is that ions might generate fault sites which propagate over large distances. In order

```
|H                      |
|OH   OH   OH   O       |
|      H    H    H      |
|___                 ___|
|                       |
|H                      |
|OH   OH   OH   OH      |
|H    H    H    H       |
```
(a) Before applying electric field.

```
  |H                        |
  |O   HO   HO   HO         |
  |     H    H    H         |
+ |___                   ___| −
  |                         |
  |H                        |
  |O   HO   HO   HOH        | ·
  |H    H    H    H         |
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(b) After six proton jumps along the direction of an applied field.

Fig. 1. Polarization resulting from proton jumps.

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[1] R. P. Auty and R. H. Cole, J. Chem. Phys. **20**, 1309 (1952).

[2] N. Bjerrum, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **27**, No. 1 (1951).

† Such fault sites would be formed, according to Bjerrum, as a result of thermal movements.

[3] S. Zaromb and R. F. Brill, J. Chem. Phys. **24**, 895 (1956).

[4] S. Zaromb, thesis, Polytechnic Institute of Brooklyn, 1954.

[5] S. Zaromb, J. Chem. Phys. **24**, 1110 (1956).

[6] R. F. Brill and S. Zaromb, Nature **173**, 316 (1954).

to show how such fault sites might be generated, use will be made of Bjerrum's model of the water molecule,[2] which appears satisfactory for the present purpose. The model consists of two positive and two negative charges of $e/6$ (e = charge of an electron) situated at the corners of a regular tetrahedron having a radius of 1 A. In the ice lattice, each such corner would face an oppositely charged corner of a neighboring tetrahedron along the line joining the centers of the tretrahedra, the distance between these corners being 0.8 A. Thus, the lattice energy of ice would consist in large part of purely electrostatic forces. The dipole moment of each tetrahedron is about 1.9 D.

II. FORMATION OF FAULT SITES AS A RESULT OF PROTON JUMPS

Let us consider now what happens to the configuration of such tetrahedra when one of them is suddenly changed to a *free* hydroxyl or hydronium ion.‡ In such a case, one of the corners of the neighboring molecules facing the ion will have the same charge as the ion and will be strongly repelled by it. A crude calculation shows that *such repulsion can readily generate a Bjerrum fault site.*§ (See Fig. 2.) *This is the basis of all the following discussion.*
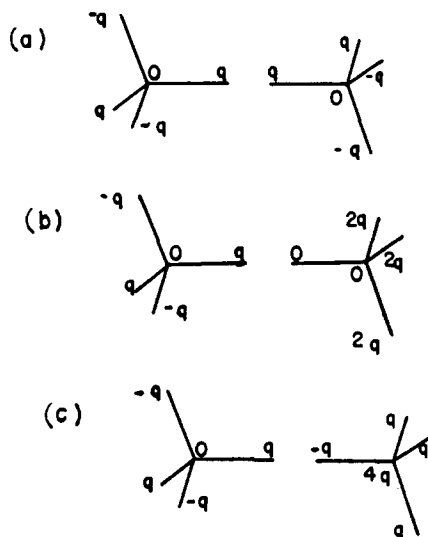

FIG. 2. Crude models for the charge distribution at a Bjerrum fault site (a) and at a freshly formed H_3O^+ ion and one of the adjacent H_2O molecules (b) and (c). (All angles are 109°. Length of each segment is 1 A. Distance between adjacent horizontal segments is 0.76 A. All charges are located at ends of segments; $q = e/6$.)

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‡ As envisioned by Bjerrum,[2] a free hydronium or hydroxyl ion would occupy the site of a normal H_2O molecule and could be displaced to an adjacent site by a proton jump.

§ The electrostatic potentials, $\Sigma q_i q_j / r_{ij}$, of the charge distributions in Fig. 2 are: (a) 0.018 e^2/A; (b) 0.026 e^2/A; and (c) 0.019 e^2/A, where q_i and q_j are charges (on different tetrahedra) separated by a distance r_{ij}, and e is the charge of an electron. Configuration (a) is that of a Bjerrum fault site, while configurations (b) and (c) are alternate models of a hydronium ion facing an oppositely charged corner of an ice molecule; although the correct electrostatic model for a hydronium ion is not known, it might be
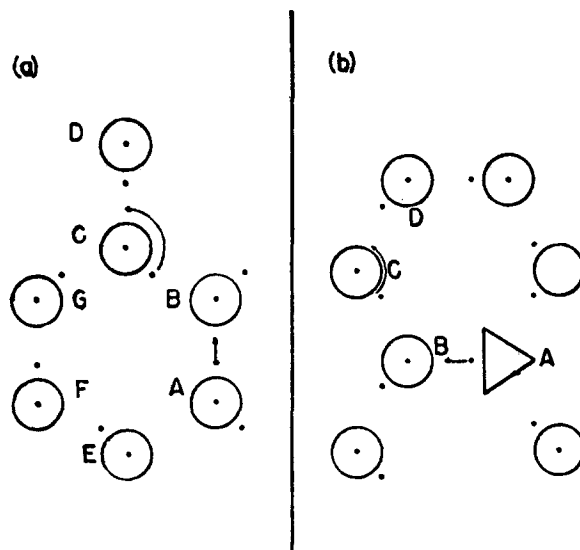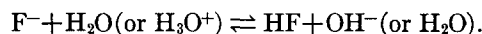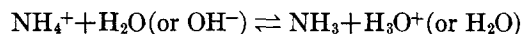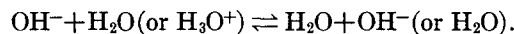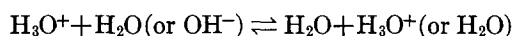

FIG. 3. Formation of fault sites as a result of proton jumps. (a) Displacement of the hydronium ion by a proton jump from A to B will cause molecule C to turn around so as to form a positive fault site between C and D or C and G. Furthermore, the initially stable configuration of molecule E will result in a negative fault site between E and A after the proton jump to B. A similar mechanism can be shown for the displacement of a hydroxyl ion. (b) A proton jump from A to B will cause molecule C to turn about so as to form a fault site between C and D. However, no additional negative fault site is formed in this case.

The NH_4^+ and F^- ions might, therefore, generate fault sites as a result of the reactions:

$$NH_4^+ + H_2O(\text{or } OH^-) \rightleftharpoons NH_3 + H_3O^+(\text{or } H_2O)$$

$$F^- + H_2O(\text{or } H_3O^+) \rightleftharpoons HF + OH^-(\text{or } H_2O).$$

Similarly, in pure ice, the remarkably high concentration of fault sites, as estimated by Bjerrum,[2] might be also due to the analogous reactions:

$$H_3O^+ + H_2O(\text{or } OH^-) \rightleftharpoons H_2O + H_3O^+(\text{or } H_2O)$$

$$OH^- + H_2O(\text{or } H_3O^+) \rightleftharpoons H_2O + OH^-(\text{or } H_2O).$$

The schematic diagrams in Fig. 3 show that two fault sites would be generated by each proton jump from an H_3O^+ *or to an* OH^- ion and only one fault site for each jump from an HF or NH_4^+ (or to an NH_3 or F^-) ion. In Fig. 3, circles (O) represent the oxygens, triangles (△) the fluorines, and dots (·) the hydrogens. A dot within a circle (⊙) represents an O–H bond pointing perpendicularly to the plane of the paper.

Considering that (a) proton jumps appear to entail the formation of fault sites, and (b) formation of fault sites requires an energy of about 10 kcal/mole,[2] it follows that a greater activation energy would be required for conductivity in ice than in water. This might be the main reason for the low intrinsic conductivity of ice, as compared with that of water.[1,7,8]

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expected to lie somewhere between the two extreme representations (b) and (c).

[7] N. E. Dorsey *Properties of Ordinary Water Substance* (Reinhold Publishing Corporation, New York, 1940).

[8] R. H. Cole, private communication.

Heretofore, this low conductivity has been attributed to possible differences between the effective microscopic dielectric constants in water and ice.[2,9,||]

Because the fault sites of opposite sign generated by the mechanism of Fig. 3a are separated by at least three molecules, they are not likely to neutralize each other immediately. On the other hand, formation of similarly separated fault sites solely by thermal motions, as envisioned by Bjerrum,[2] would require (a) about the same activation energy as that of a proton jump (energy required to form two fault sites); and (b) the successive rotation of three neutral molecules. The probability of such successive rotations would be extremely small, because the molecules would tend to turn back so as to neutralize the fault sites both after the first and after the second rotation.

Whether proton jumps are of importance in the dielectric relaxation *in pure ice* will depend, however, on the existence of free H_3O^+ and OH^- ions in ice in sufficient concentrations. This possibility will be examined in Sec. III. The possibility that proton jumps may be responsible for the observed relaxation rates in ice-NH_4F solutions will be examined in Sec. IV.

III. TESTS OF THE PROPOSED MECHANISM IN PURE ICE

A. Orders of Magnitude

If proton jumps actually are the major cause of the formation of fault sites in pure ice as well as in ice-NH_4F solutions, then it might be interesting to estimate the frequency of proton jumps necessary to account for the observed rates of dipole turns. The latter may be set equal to $1/\tau^*$, where τ^* is the intrinsic (or Debye) dielectric relaxation time. Following Bjerrum,[2] we shall set:

$$1/\tau^* = 2\nu(p+n)e^{-E_f/RT}, \quad (1)$$

where ν is the frequency of hindered rotation in ice, p and n are the numbers of negative and positive fault sites per molecule, respectively, and E_f is the activation energy for the displacement of a fault site to one of the neighboring bonds. According to Fig. 2, the rate of formation of a set of negative and positive fault sites, R_f, is equal to that of proton jumps, R_p:

$$R_f = R_p. \quad (2)$$

Bjerrum[2] showed that $R_p = 3.8 \times 10^{10}\sigma$, (3)

where σ is that part of the specific conductance of ice which can be attributed to proton jumps.

[9] Schellman, Ph.D. thesis, Princeton University, 1950.

[||] Bjerrum[2] suggests that this effective dielectric constant may be fifteen times lower than in water; hence, the energy required to form a pair of free H_3O^+ and OH^- ions would be over 30 kcal/mole in ice, as compared with the 13.7 kcal/mole in water. However, there does not seem to be sufficient justification for assuming such a tremendous difference between these effective dielectric constants. A difference by a factor of three, rather than fifteen, might be justified, according to section IV (D) of this paper. Such a difference would cause only a small increase (2.6 kcal/mole) in the energy required to separate two ions.

At equilibrium, R_f must be equal to the rate of disappearance of fault sites, R_d:

$$R_f = R_d. \quad (4)$$

To estimate R_d we shall estimate the frequency of encounters of positive and negative fault sites. We shall assume that two opposite fault sites will disappear whenever they enter into the following configuration (I):

$$\cdot \odot \quad \odot \cdot$$
$$\odot \quad \cdot \quad \cdot \quad \odot$$
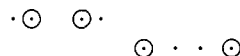
because, then, the two intermediate molecules will automatically flip over. Let us, therefore, consider the configurations (II):

$$\cdot \odot \quad \cdot \odot$$
$$\odot \cdot \quad \cdot \odot \quad \quad \odot \cdot$$
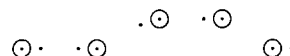
Let z_{II} = frequency of co-ordinations (II),

$$f = \text{frequency of turns/fault site} = 2\nu e^{-E_f/RT}, \quad (5)^2$$

then the rate of disappearance of fault sites is

$$R_d = z_{II}/6 \quad (6)$$

since only one out of six possible rotations at a fault site will lead to configuration I. To find z_{II}, let θ = average fraction of time which a fault site P is in configuration (II) with respect to a fault site N.

$$\theta = \frac{\text{No. of positions II around fault site } P}{\text{total No. of positions/fault site } N}$$

$$\simeq \frac{2^4}{2/n} = 8n. \quad (7)\P$$

Then,

$$z_{II} = f\theta p \quad (8)$$

and

$$R_d = 8fnp/6 \simeq 2\nu np e^{-E_f/RT} = 2\nu n^2 e^{-E_f/RT}, \quad (9)\P$$

assuming

$$p = n. \quad (10)$$

Equations (4) and (9) yield:

$$R_d = R_f = 2\nu n^2 e^{-E_f/RT}. \quad (11)$$

Hence, Eq. (1) becomes:

$$1/\tau^* = 4n\nu e^{-E_f/RT} = (8\nu e^{-E_f/RT} R_f)^{\frac{1}{2}}. \quad (12)$$

Equations (2), (3), and (12) then yield:

$$1/\tau^* \simeq (3 \times 10^{+11}\sigma\nu e^{-E_f/RT})^{\frac{1}{2}}. \quad (13)$$

Bjerrum[2] estimates E_f at 2.5 kcal/mole. At 0°C:

$$1/\tau^* = 8.3 \times 10^5 \text{ sec}^{-1} \quad e^{-E_f/RT} \simeq 10^{-2}$$
$$\nu = 2.4 \times 10^{13} \text{ sec}^{-1}.^2$$

¶ Only orders of magnitude are of interest here, not the exact figures.

Hence, Eq. (13) yields:

$$\sigma = \frac{(8.3 \times 10^5)^2}{3 \times 10^{11} \times 2.4 \times 10^{13} \times 10^{-2}} = 10^{-11} \text{ ohm}^{-1} \text{ cm}^{-1}.$$

This is 250 times smaller than the value used by Bjerrum[2] for the static conductivity of ice, and about 1000 times lower than in pure water. If the Lorentz correction were omitted in the above calculation, then: $1/\tau^* = 4 \times 10^4 \text{ sec}^{-1}$ and $\sigma = 2.5 \times 10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$; i.e., smaller by an additional factor of 400. The experimental values of static conductivity referred to by Bjerrum are about five times higher than those found by Auty and Cole,[1] and even the latter probably do not represent the intrinsic porton jump conductivity of ice, as can be inferred from the irreproducibility of the experimental results.[8] Thus, while the value of σ estimated here cannot serve as a conclusive test of any theory due to the unfortunate absence of adequate proton jump conductivity data, it does at least not appear unreasonable.

B. Activation Energies

If E_c is the activation energy for proton jump conductivity, i.e., $\sigma = \text{constant} \times e^{-E_c/RT}$, then according to Eq. (13) one should get $E_d = (E_c + E_f)/2$, where $E_d(13.2 \text{ kcal/mole})^1$ is the activation energy for dielectric relaxation. Since $E_f \simeq 2.5 \text{ kcal/mole},^2$ E_c should approximately equal 24 kcal/mole.

To estimate E_c one may use statistics similar to those of Sec. 3A. In this case, however, three different energies should be considered: I—the energy of ionization of two adjacent molecules, A—the activation energy for the neutralization of two adjacent ions, and S—the energy required to separate two adjacent ions by an infinite distance. Then $(I+A)$ would represent the activation energy for ionization. Hence, the rate of ionization $= k_1 e^{-(I+A)/RT} =$ the rate of disappearance of ions $= k_2 e^{-(A-S)/RT}[H_3O^+]^2$, where k_1 and k_2 are constants. Hence, the ion concentration is:

$$[H_3O^+] = (k_1/k_2)^{\frac{1}{2}} \exp[-(I+S)/2RT].$$

Then, if P_I is the activation energy for a proton jump in ice, the rate of proton jumps will be:

$$R_p = (k_1/k_2)^{\frac{1}{2}} k_I \exp[-(P_I + \tfrac{1}{2}I + \tfrac{1}{2}S)/RT],$$

where k_I is the frequency factor for the rate of proton jumps in ice. Hence, one should have:

$$P_I + \tfrac{1}{2}I + \tfrac{1}{2}S = E_c \simeq 24 \text{ kcal/mole}.$$

Assuming that the effective microscopic dielectric constant in ice is about one third that of water at 0°C (see Sec. IVD), and that I is the same in ice as in water, one obtains $I + S \simeq 16 \text{ kcal/mole}$. Hence, $P_I \simeq 24 - 16/2 \simeq 16 \text{ kcal/mole}$. This should be equal to the activation energy for a proton jump in water, P_w, plus the energy F required to form a pair of fault sites according to

the mechanism of Fig. 3a. Bjerrum[2] estimates P_w at 3 kcal/mole. Hence, one may set $F \simeq P_I - P_w \simeq 13 \text{ kcal/mole}$. This is about 40% lower than the value expected from Bjerrum's estimates[2] of the energy required to form two fault sites (21 kcal/mole). This disagreement could be accounted for by the following possibilities: (1) The effect of polarizability and of increased distance between the mutually repelling charges at a fault site may have been underestimated by Bjerrum. (2) In the mechanism of Fig. 3a, the fault sites resulting from the proton jump may require less energy because of the presence of an ion in a second neighbor position. (3) If the net repulsive forces in Figs. 2b and c have been somewhat overestimated, then the proton jump shown in Fig. 3a may not result *immediately* in a fault site between molecules C and D but could give rise, instead, to an intermediate configuration requiring a somewhat lower energy than that of a fault site.**

C. Frequency Factors

According to Sec. 3A, the ratio of the rates of proton jumps in ice and water should be no less than $1 : (4 \times 10^{-5})$. Hence, $(R_p)_I/(R_p)_w = (k_I/k_w)e^{-(P_I - P_w)/RT} \times [H_3O^+]_I/[H_3O^+]_w \geq 3 \times 10^{-6}$, where the subscripts I and w refer to ice and water, respectively. According to the estimates of the preceding section, $P_I - P_w \simeq 13$ kcal/mole. On the other hand, the frequency factors generally follow the same trend as the activation energies. Thus, for gaseous molecules, the frequency factor would be proportional to $(E/RT)^{s-1}$, where s is the number of vibrational degrees of freedom in the molecule.[10] In the condensed phases, s should be larger than in the gas, partly because the translational and rotational modes of motion change into oscillatory modes, and partly because of cooperative effects between adjacent particles. If s were only equal to all the degrees of freedom of one H_3O^+ ion, then the factor (k_I/k_w) would be approximately $(16/3)^{11}$ or 10^8, whereas $\exp[-(P_I - P_w)/RT]$ would be about 3×10^{-11}. This would require that $[H_3O^+]_I/[H_3O^+]_w$ be no less than 10^{-3}. Unless the effective microscopic dielectric constant in ice is much smaller than 30, there is little reason for expecting $[H_3O^+]_I$ to be much less than 10^{-10} mole/l.

IV. TESTS IN ICE-NH₄F SOLUTIONS

A. Proton Jumps To and From the Solute Ions in Aqueous Solutions

Before considering the behavior of NH₄F in ice, it might be worthwhile to gather the pertinent information about its behavior in aqueous solutions, for which more experimental data are available.

** Such a configuration would be unstable and would still give rise to a fault site before the ion is displaced to a new position; the controlling step, however, would require less energy than a mechanism involving the immediate formation of two fault sites.

[10] K. J. Laidler, *Chemical Kinetics* (McGraw-Hill Book Company, Inc., New York, 1950), pp. 80–81.

The dissociation constants of H_2O, NH_3, and HF at 25°C are:

$$K_w = [OH^-][H_3O^+] = 10^{-14}\left(\frac{\text{moles}}{\text{liter}}\right)^2,$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.7 \times 10^{-5}\frac{\text{moles}}{\text{liter}},$$

and

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = 3.2 \times 10^{-4}\frac{\text{moles}}{\text{liter}}.$$

Hence,

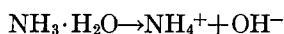$$[H_3O^+] = (K_w K_a/K_b)^{\frac{1}{2}} = 4.3 \times 10^{-7} \text{ moles/liter},$$

$$[OH^-] = (K_w K_b/K_a)^{\frac{1}{2}} = 2.3 \times 10^{-8} \text{ moles/liter},$$

and

$$\frac{[HF]}{[F^-]} = \frac{[H_3O^+]}{K_a} = \frac{4 \times 10^{-7}}{3.2 \times 10^{-4}} = \frac{1}{800},$$

$$\frac{[NH_3]}{[NH_4^+]} = \frac{[OH^-]}{K_b} = \frac{2.3 \times 10^{-8}}{1.7 \times 10^{-5}} = \frac{1}{700}.$$

This means that, on the average, each ammonia will be a neutral NH_3 molecule during 1/700-th of the time. Now, the rate of the reaction

$$NH_3 \cdot H_2O \rightarrow NH_4^+ + OH^-$$

was found by sound absorption measurements to be $4 \times 10^5/\text{sec}/NH_3$ molecule.[11] Hence, at equilibrium, the rate, R_a, of proton jumps from NH_4^+ ions in a solution of NH_4F must be

$$R_a = (1/700) \times 4 \times 10^5 = 600/\text{sec/ion}.$$

It might be interesting to compare this last value with the rate, R_{OH^-}, of the reaction

$$H_2O + OH^- \rightarrow OH^- + H_2O,$$
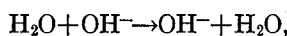
i.e., to the rate of displacements of a hydroxyl ion to a neighboring site. This can be estimated with the aid of the equation[2]

$$R_{OH^-} = 6 \times 10^{-7} \lambda_{OH^-} RT/\bar{\Delta}^2 F^2 = 5.35 \times 10^{-9} T \lambda_{OH^-}/\bar{\Delta}^2$$

displacement/sec/ion, where λ_{OH^-} is the equivalent conductance of the OH^- ion, $\bar{\Delta}$ is the distance between two adjacent water molecules, and F is the Faraday. Setting $\bar{\Delta} = 2.76 \times 10^{-8}$ cm and $\lambda_{OH^-} = 198$ liter/(ohm-cm-mole), one obtains for 298°K:

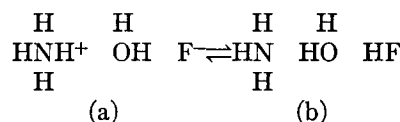$$R_{OH^-} = 4.1 \times 10^{11} \text{ displacements/sec/ion}$$
$$= 4.1 \times 10^{11} \times 2.3 \times 10^{-8}/55$$
$$= 170 \text{ displacements/sec/}H_2O$$

molecule in an NH_4F solution.

A comparison of R_a with R_{OH^-} suggests that neutralization of an NH_4^+ ion occurs only when one out of

[11] M. Eigen, Z. physik. Chem., Neue Folge 1, 176 (1954).

three or four sites happens to be occupied by a hydroxyl ion. In other words, an NH_4^+ ion could hardly be expected to give off a proton in the absence of an oppositely charged ion nearby. The same will be assumed to hold also for the capture of a proton by a F^- ion. Hence, any increase in the rate of proton jumps in water or ice upon addition of NH_4F could only be due to pairs of NH_4^+ and F^- ions. Furthermore, it is hard to see how a proton jump between adjacent ions could generate a fault site in ice. If, on the other hand, the ion pair is separated by more than one ice molecule, frequent proton jumps between the ions could hardly be expected to occur. It is, therefore, proposed that a source of fault sites in ice-NH_4F solutions might consist of an ion pair separated by a single ice molecule giving rise to an alternate configuration consisting of three neutral molecules.

$$\begin{array}{ccccc}
\text{H} & \text{H} & & \text{H} & \text{H} \\
\text{HNH}^+ & \text{OH} & \text{F} \rightleftharpoons \text{HN} & \text{HO} & \text{HF} \\
\text{H} & & & \text{H} & \\
\text{(a)} & & & \text{(b)} &
\end{array}$$

Although it was shown in the foregoing that, in water at 25°C, NH_4^+ and F^- ions will be in the form of NH_3 and HF for only 1/700th and 1/800th parts of the time, respectively, the electrostatic attraction between the opposing ions is bound to shift the equilibrium partly towards configuration (b). However, the foregoing comparison between R_{OH^-} and R_a suggests that, in water at least, configuration (a) will still be quite frequent (probably the more frequent one), as otherwise the ratio of R_a to R_{OH^-} should have been several times greater than found above.[††] In other words, the electrostatic interaction between the ion pair appears more likely to reduce the energy difference between configurations (a) and (b) than to raise another energy barrier.

B. Orders of Magnitude

In a dilute solution containing X moles of NH_4F per mole of ice, the number of ion pairs in second neighbor configurations, N_{13}, will be:

$$N_{13} = 12X^2 e^{-V/kT} \text{ ion pairs/ice molecule,} \quad (14)$$

where V is the electrostatic potential energy of a second-neighbor ion pair. The factor $12X^2$ represents the *unweighted* probability, $12X$, that an NH_4^+ ion will be in one of the 12 second-neighbor sites around a F^- ion, multiplied by the concentration, X, of F^- ions. With moles per liter as concentration units, Eq. (14) would take the following form, according to the Deybe-Hueckel theory:

$$c_{13} \simeq (12/50)c^2 \exp[e^2 e^{-k(r_{13}-a)}/DkTr_{13}(1+\kappa a)] \quad (15)$$

[††] If the presence of an OH^- ion in a second nearest site from an NH_4^+ ion had always resulted in neutralization of the ions, then the ratio of R_a to R_{OH^-} would be equal to the number of second nearest molecules around the ion; i.e., to more than 12:1.

where $\mathbf{e}$ is the charge of an electron, D the effective microscopic dielectric constant of the medium, k the Boltzmann constant, r_{13} the distance between second-neighbor sites $(4.5\times10^{-8}\text{cm})$, a the distance between adjacent sites $(2.76\times10^{-8}$ cm$)$, and $1/\kappa$ the thickness of the ion atmosphere.[12]

For very dilute solutions, k approaches zero, and Eq. (15) simplifies to:

$$c_{13}\simeq(12/50)c^2\exp[e^2/DkTr_{13}].\qquad(16)$$

If the Debye-Hueckel theory does not apply to ice-NH$_4$F solutions, then Eq. (16) would also represent the other extreme, namely the complete absence of a shielding ion-atmosphere. In dilute solutions, both extreme possibilities converge to the same relation, hence it can be used regardless of the applicability of the Debye-Hueckel theory. For intermediate concentrations, Eq. (16) and (15) show analogous trends, although the numerical results differ.

Assuming that $D\simeq30$ in ice, application of Eq. (16) and (12) to the experimental results of Zaromb and Brill[3] shows that at 0°C, 5000 fault sites/sec would have to be generated by an ion pair, if the questionable Lorentz correction ought to be included in the calculations, and only 10 fault sites/sec if this correction ought to be omitted.

C. Activation Energies

According to Fig. 3b a proton jump from an NH$_4^+$ ion or HF to an adjacent H$_2$O molecule (or OH$^-$ ion) or from an H$_2$O molecule (or H$_3$O$^+$ ion) to an adjacent NH$_3$ or F$^-$ ion would generate one fault site. This would require at least 6.5 kcal/mole (F/2), according to Sec. 3B.

The observed activation energy for dielectric relaxation in ice-NH$_4$F solutions is about 4 kcal/mole. Hence, according to Eq. (12), the apparent activation energy for fault-site formation would be about 5 kcal/mole. This last value would represent the difference between the actual activation energy required for the formation of a fault site near an ion pair, A_I, and the value of e^2/Dr_{13} in Eq. (16). For $D=30$, e^2/Dr_{13} would be about 2.5 kcal/mole, and A_I would exceed $F/2$ by about 1 kcal/mole.

If Eq. (15) is applicable to ice-NH$_4$F solutions, then the apparent activation energy should vary slightly with concentration. Although this might be indicated from the experimental points of Zaromb and Brill,[3] more accurate measurements will be necessary to resolve this question.

D. Frequency Factors

According to the picture presented in the preceding sections, the rate of fault-site formation, R_f, should be

proportional to the concentration, c_{13}, of second-neighbor ion-pairs. Hence, according to Eq. (12) the frequency factor for dielectric relaxation rates should be proportional to $c_{13}^{\frac12}$.

However, the value of c_{13} obtained from Eq. (15) or (16), would also include those second-neighbor pairs which may be adjacent to a third ion; i.e., the configurations NH$_4^+$F$^-$H$_2$O NH$_4^+$ and F$^-$ H$_2$O NH$_4^+$ F$^-$. In such configurations, it appears likely that proton jumps between the second-neighbor ions may be largely prevented by the interactions between the adjacent ions. Hence, if c_{13}' is the concentration of those second-neighbor pairs which are free from any adjacent ions, the corrected from of Eq. (15) becomes:

$$c_{13}'\simeq\frac{12}{50}(c-c_{12})^2\exp\left[\frac{\mathbf{e}^2e^{-\kappa(r_{13}-a)}}{DkTr_{13}(1+\kappa a)}\right]\qquad(17)$$

$$\simeq\frac{12}{50}\left(c-\frac{4}{50}c^2e^{e^2/DkTa(1+\kappa a)}\right)^2\exp\frac{\mathbf{e}^2e^{-\kappa(r_{13}-a)}}{DkTr_{13}(1+\kappa a)},\qquad(18)$$

where c_{12} is the concentration of adjacent pairs.

Equation (18) can lead to maximum values of c_{13}'. If the values of D and κ for water at 0°C are used, the deviative dc_{13}'/dc vanishes for $c\sim1$ mole/liter.‡‡ If a three-times smaller value is used for D (which also increases κ by a factor of 3), then dc_{13}'/dc vanishes for $c\sim0.01$ mole/liter.

These last two orders of magnitude seem very relevant to the experimental results of Zaromb and Brill,[3] Brill and Zaromb,[6] and Ender and Brill,[13] obtained with freshly frozen samples, samples stored for 24 hr at -78.5°C, and samples stored for 36 hr or more at $-3°$ to -6°C, respectively. Minimum relaxation times, and, therefore, highest rates of dipole turns, were indicated for concentrations of about 0.1, 0.025, and 0.01§§ mole/l, respectively. This variation with storage would appear very puzzling at first sight, considering that the phase diagram for the system ice-NH$_4$F[3,4,6] shows that: (a) any inhomogeneities in sample compositions arising during freezing could not account for such large differences; and (b) any such inhomogeneities would be greatest with the dilute solutions, which, however, showed little change, if any, with storage.

On the other hand, the observed variations would be in agreement with Eq. (18) if the effective microscopic dielectric constant in ice is about a third of that in water. This appears reasonable, because the electrostatic field of each ion cannot be shielded as effectively in the relatively rigid ice structure as by the more

[12] G. Scatchard, in E. J. Cohn and J. T. Edsall, *Proteins, Amino-Acids and Peptides* (Reinhold Publishing Corporation, New York, 1943), p. 55.

‡‡ If κ were set equal to zero, as in Eq. (16), then dc_{13}'/dc would vanish for $c\sim0.5$ mole/liter (in water at 0°C). Similarly the subsequent estimates would have to be modified, but the basic arguments would not be affected.
[13] R. F. Brill (personal communication).
§§ The last value is roughly estimated by extrapolation of data for much higher and lower concentrations.

TABLE I. Correlation between the rate of dipole turns and the estimated concentration of second-neighbor ion pairs.

c moles/liter	$10^3 c_{13}'^{\frac{1}{3}}$ (moles/liter)$^{\frac{1}{3}}$	$\tau \times 10^3$ sec	$10^{-3}/\tau$ sec^{-1}	$10^{-6}/\tau c_{13}'^{\frac{1}{3}}$ sec^{-1}(moles/ liter)$^{-\frac{1}{3}}$
0.0005	1.2	0.173	5.8	5.0
0.0015	3.1	0.070	14.3	4.7
0.00375	7.1	0.0435	23	3.2
0.0125	20	0.0171	58.5	3.0
0.0375	45	0.0060	167	3.7
0.10	85	0.0026	385	4.5

freely oriented molecules in water (see also reference ||). According to this interpretation, then, the average distances between NH_4^+ and F^- in freshly frozen solutions would be intermediate between those in aqueous and those in solid solutions of the same concentration of NH_4F.

Beside explaining the observed maxima in dielectric relaxation rates, Eq. (18) can also be used to correlate the rates observed by Zaromb and Brill[3] with c_{13}'. Using half the value in water for D (and, therefore, a value $\sqrt{2}$ times larger for κ) at 0°C, the values of $c_{13}'^{\frac{1}{3}}$ listed in the second column of Table I are obtained for concentrations of 0.0005 to 0.10 mole/l (or 0.002 to 0.4 weight percent). The second column of that table lists the corresponding values of τ obtained from the results of Zaromb and Brill[3] for the temperature of 250°K. The ratio of $1/\tau$ to $c_{13}'^{\frac{1}{3}}$ obtained in the last column ranges between 3.0×10^6 and 5.0×10^6 sec^{-1} (1/mole)$^{\frac{1}{3}}$, which can be considered constant within the accuracy of the experimental data and of the assumptions made in calculating c_{13}'.

For concentrations higher than 0.10 mole/l, the simple Debye-Hückel theory breaks down completely, hence Eq. (18) is not applicable, and the variation of c_{13}' with c is difficult to estimate. However, it may be expected that once the maximum value of c_{13}' has been reached, a further increase in c will increase the concentration of adjacent ion pairs at the expense of free second-neighbor pairs. If it could be assumed that, in the high concentraion range,

$$c_{13}' \simeq K/c, \tag{19}$$

where K is a constant, then a proportionality would again be indicated between $c_{13}'^{\frac{1}{3}}$ and $1/\tau$, as shown in Table II.

V. CONCLUSIONS

In pure ice, the formation of Bjerrum fault sites as a result of proton jumps is suggested by electrostatic considerations. This can be used to explain (a) the low proton jump conductivity in ice, as compared with that in water, and (b) the likely presence of Bjerrum fault sites in pure ice in rather high concentrations. Although the estimates of frequency factors and activation energies based on the proposed proton jump mechanism are too crude to serve as evidence in its favor, they show at least no serious disagreement with known facts.

TABLE II. Apparent correlation between the rate of dipole turns and the inverse square root of concentration in the high concentration range.

c moles/liter	$\tau_{250°K} \times 10^3$ sec	$10^{-5}c^{\frac{1}{3}}/\tau$
0.10	0.0026	1.22
0.25	0.0041	1.22
2.5	0.0135	1.17

In ice-NH_4F solutions, proton jumps between an NH_4^+-F^- ion-pair in second-neighbor sites may also induce fault sites in a neighboring water molecule. This mechanism seems to explain the low activation energy observed for the dielectric relaxation rates, as well as the peculiar concentration dependence of the frequency factor for these rates. Furthermore, the marked changes in frequency factor observed upon storing freshly frozen concentrated ice-NH_4F samples can also be explained in terms of this picture.

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