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# Electrical Properties of Ice Doped with Different Electrolytes

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## Abstract

The electrical properties of ice doped with the series of hydracids from HF to HI, with  $\text{NH}_3$  and with  $\text{NH}_3$  and HF in different ratios were studied.

In most cases the DC conductivity was measured. The similarity of the results obtained under these conditions for ice doped with different hydracids indicates that these monovalent anions play a similar role in the crystal lattice in spite of their different diameters.

A comparison of the behaviour of the ice+HF+ $\text{NH}_3$  system with that of ice+HF and ice+ $\text{NH}_3$  shows that, as a first approximation, the general laws of electrolytes may be applied to doped ice. An estimation is obtained of the dissociation constants involved and of the ratio  $\mu_-/\mu_+$  between the mobility of  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  ions.

Ice doped with  $\text{NH}_3$  and, in a few cases, ice doped with  $\text{NH}_4\text{F}$  were also studied by an AC method. The results indicate that the concentration in the lattice of Bjerrum defects of D type is slightly increased by the presence of  $\text{NH}_3$ . An estimation was obtained of the corresponding dissociation constants and of the ratio  $\mu_D/\mu_L$ , between the mobility of D and L defects. The estimation shows that  $\mu_D/\mu_L < 1$ . This may be caused by the higher formation energy of the D defects than that of the L defects.

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## I. Introduction

The electrical properties of ice are related to the presence of certain types of lattice defects, *i.e.* of ions  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$  and of Bjerrum defects D, L (doubly occupied and vacant bonds) and it was established that the proton mobility is several orders higher than the usual mobility of ions in solids. Thus, the presence of electrolytes may substantially modify the electric properties of the crystals only if it modifies the concentration of these defects.

The most thorough studies of the electric behaviour of doped ice were performed with HF as the dopant (Gränicher, 1963; Jaccard, 1959). This electrolyte has been accepted to be one of the most suitable lattice modifiers because of the similarity in diameter and number of electrons between F and O atoms. Thus HF may be considered to replace  $\text{H}_2\text{O}$  molecules in the lattice, increasing the concentration of  $\text{H}_3\text{O}^+$  ions and L defects in accordance with the following processes



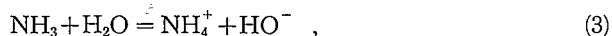
In eq. (2) we have used Onsager's notation (Onsager and Dupuis, 1960; Onsager,

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1962) for the association of HF with a D defect and the corresponding dissociation of the vacant hydrogen bond created in the lattice by the structure of this molecule.

A symmetrical behaviour could be expected for ice doped with  $\text{NH}_3$ ; actually also N and O atoms are similar in diameter and  $\text{NH}_3$  molecules (or  $\text{NH}_4^+$  ions) may be assumed to enter the ice lattice substitutionally with respect to  $\text{H}_2\text{O}$ , giving place to the processes analogous to eqs. (1) and (2):



On the other hand, studies of impurity segregation of ice growing from different electrolytic solutions (Jaccard and Levi, 1961; De Micheli and Iribarne, 1963) have shown that neither the ratio between the solid and liquid concentration (segregation factor S) nor the value of maximum concentration which may be obtained in ice, are mainly determined by the diameter of the impurity atoms. Actually the factor S has the same order of magnitude for all the hydracids from HF to HI (Levi and Arias, 1964) (between 50 and 500 according to concentration, with a maximum near  $10^3$  for ice doped with HI) though the atomic diameter of the anion increases from 1.36 to 2.16 Å; on the contrary, the segregation is much higher for  $\text{NH}_3$  (up to  $10^4$ ) in spite of the observed similarity in diameter between N and O.

In the present work the electric behaviour of doped ice is discussed in the following cases:

1) Ice doped with the series of the hydracids, from HF to HI, to investigate the importance of the atomic diameter in the role played by the impurity molecules in the lattice;

2) Ice doped with  $\text{NH}_3$  to obtain information on the processes given by eqs. (3) and (4) and on the mobility of  $\text{OH}^-$  ions and D defects;

3) Ice doped with HF and  $\text{NH}_3$  in different ratios, which was assumed to allow a direct comparison between the values of the three dissociation constants involved (of the acid, the base and of ice considered as a solvent) and between the mobility of defects of opposite sign, *i.e.* of ions  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  and of Bjerrum defects D and L.

## II. Results and Discussion

### EXPERIMENTAL METHODS

Ice was grown in polyethylene tubes approximately 2.4 cm in diameter by immersion in a bath of cold alcohol, at a speed of 0.5 to 4  $\mu$ /sec. In most cases the solution was gently stirred during growth to maintain a homogeneous concentration. Ice doped with  $\text{NH}_3$  was better obtained without stirring.

The actual concentration of the electrolyte in the samples was measured after melting. Generally the concentration was determined by the measurement of electrical conductivity of melted ice, using a calibrated conductivity cell. In the case of ice doped with HF and  $\text{NH}_3$  in different ratios, the amperometric titration and the Nessler method were used for the determination of the concentrations of  $\text{F}^-$  and  $\text{NH}_4^+$  respectively. As an auxiliary method, pH measurements were also performed.

For the electrical measurements in ice, Pt electrodes were mounted on the surface

of the sample by heating in such a way as to allow the surface to melt slightly and refreeze.

To reduce the errors due to the formation of the space charges near the electrodes, the DC measurements were usually made by an oscillograph used as a voltmeter, so that the instantaneous voltage, when the field was applied, could be determined on a known resistance connected in series with the ice. In high concentrations of the electrolytes, especially for ice doped with  $\text{NH}_3$ , the transient effects were negligible and a galvanometer could be used for the measurements.

Potential differences of 45 to 90 V were applied on samples usually about 1 cm thick. In the special case of ice doped with  $\text{HF} + \text{NH}_3$  samples up to 3–4 cm of thickness were used to make possible the more complex analysis of the melted ice.

For the AC measurements we used a General Radio Capacitance Bridge (model 1610-3) including a guard circuit which eliminates the capacitance of the enclosure and leads connected to the unknown capacitor. Owing to the low capacitance and high dissipation factor of the ice samples, the "substitution method" was used, where the unknown capacitor is connected across the precision capacitor of the bridge.

Before beginning the measurements, the samples, were maintained for several hours at the desired temperature.

## RESULTS

### a) *Ice doped with hydracids*

The results obtained in ice doped with hydracids (Levi and Arias, 1964) are plotted in Fig. 1, curve (1). In Fig. 1, the logarithm of the conductivity  $\sigma$  of different samples is plotted against the logarithm of the concentration  $C$ , at  $t = -17^\circ\text{C}$ . It may be noted that all of the experimental values corresponding to the different hydracids are distributed along the same curve.

In low concentrations, the curve may be considered as a straight line with a slope equal to 1/2. In this range, the conductivity may be expressed by

$$\sigma = \tau C^{1/2}, \quad (5)$$

where  $\tau = 5 \times 10^{-15} \text{ ohm}^{-1} \text{ cm}^{1/2}$ . For concentrations between  $5 \times 10^{-4}$  and  $10^{-2} \text{ N}$ , the experimental points deviate from the straight line and are scattered along the inferior branch of the curve, which seems to tend to have a constant value. In the range of higher concentrations, the conductivity increases again, showing the distribution expressed by the eq. (5). However, the results are more dispersed in this region and the ice begins to lose its transparency.

Some experiments were also performed using acids of more complex molecules and different valence, such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{BO}_3$ . It was observed that the behaviour of ice doped with  $\text{HNO}_3$  was similar to that of ice doped with hydracids. The concentration obtained in ice grown from solutions of  $\text{H}_2\text{SO}_4$  was less reproducible and the values of conductivity of doped ice was lower and more dispersed than that of hydracids. As for  $\text{H}_3\text{BO}_3$ , its dissociation in water is low and it does not change the conductivity of ice in a measurable way.

These results indicate that monovalent anions of very different structure and diameter, such as  $\text{F}^-$  and  $\text{NO}_3^-$  may play a similar role in the crystal lattice. As for  $\text{H}_2\text{SO}_4$ , probably

similar mechanisms may exist which bring about the dispersion of the results, both in segregation and conductivity.

It is interesting to note that these results have been recently confirmed by Gross (1965) who obtained, for ice doped with HF, a curve of conductivity at  $-15^{\circ}\text{C}$ , which nearly coincides with the curve of Fig. 1 for concentrations  $<10^{-2}\text{N}$ . Gross is of the opinion that only the straight part of the curve is significant and represents his results by a law of the type (5) with  $\tau = 1 \times 10^{-4} (\text{mol/l})^{-1/2} \text{ohm}^{-1} \text{cm}^{-1} = 4 \times 10^{-15} \text{ohm}^{-1} \text{cm}^{1/2}$ . This author considered that the divergence of data from the straight line observed in high concentrations resulted from intergranular precipitation of the electrolyte, which caused the opacity of the samples. However, a careful analysis of the experimental results given by Gross indicates that the change of slope of the curve begins, as in our case, in concentrations near  $5 \times 10^{-4}\text{N}$ , where ice generally is observed to be transparent. This behaviour will be discussed later. In the present paragraph, we suggest that the reproducibility of results in crystals obtained in different growth conditions may indicate the possibility that the increase of conductivity in high concentrations could be limited by some effects closely related to the structure of the lattice.

b) *Ice doped with  $\text{NH}_3$*

The electrical behaviour of ice doped with  $\text{NH}_3$  has been studied by AC (Arias *et al.*, 1966) and DC (Levi and Lubart, 1961) methods.

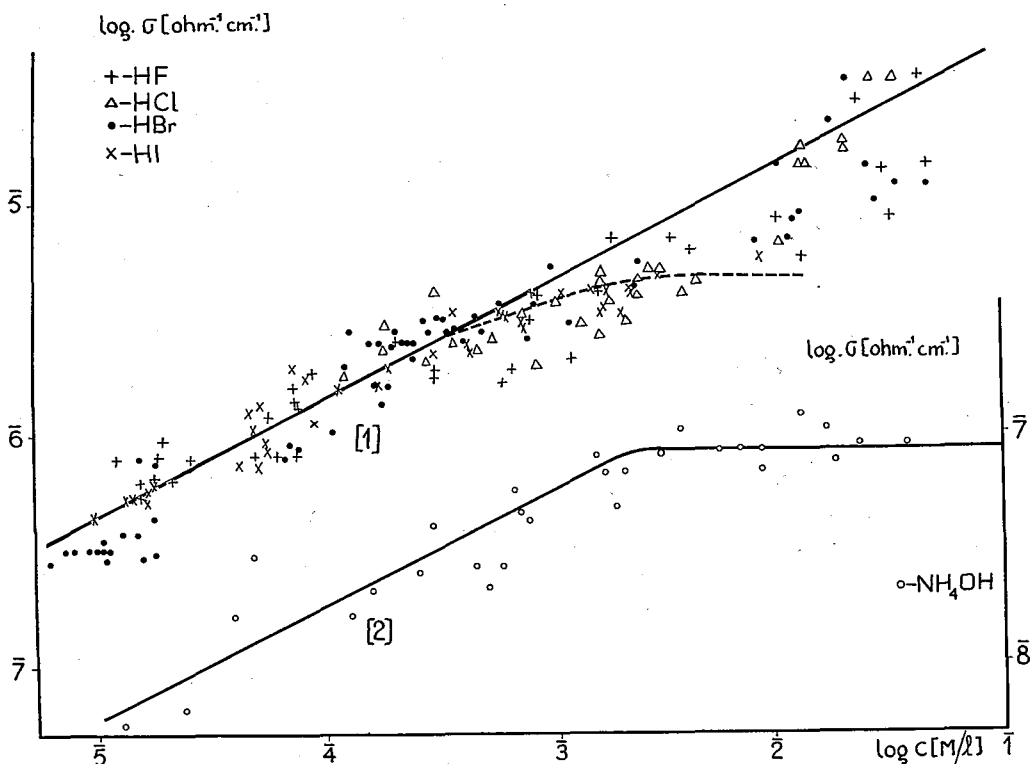


Fig. 1. DC conductivity of ice doped with hydracids (curve 1) and with  $\text{NH}_3$  (curve 2) as a function of concentration

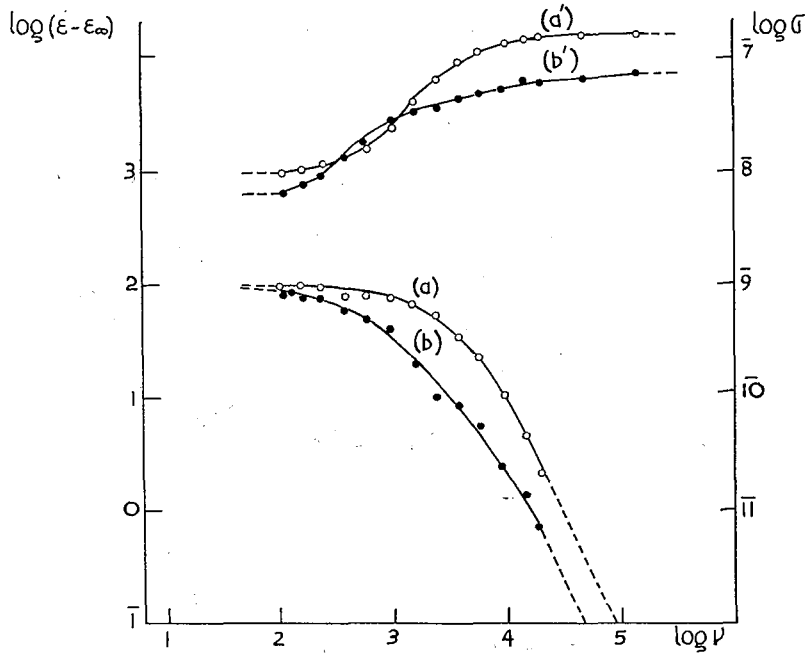


Fig. 2. Ice doped with  $\text{NH}_3$ ,  $C=8 \times 10^{-5}$  N. Curves (a) and (b), dielectric constant and curves (a') and (b'), conductivity at  $-10$  and  $-25^\circ\text{C}$ , respectively

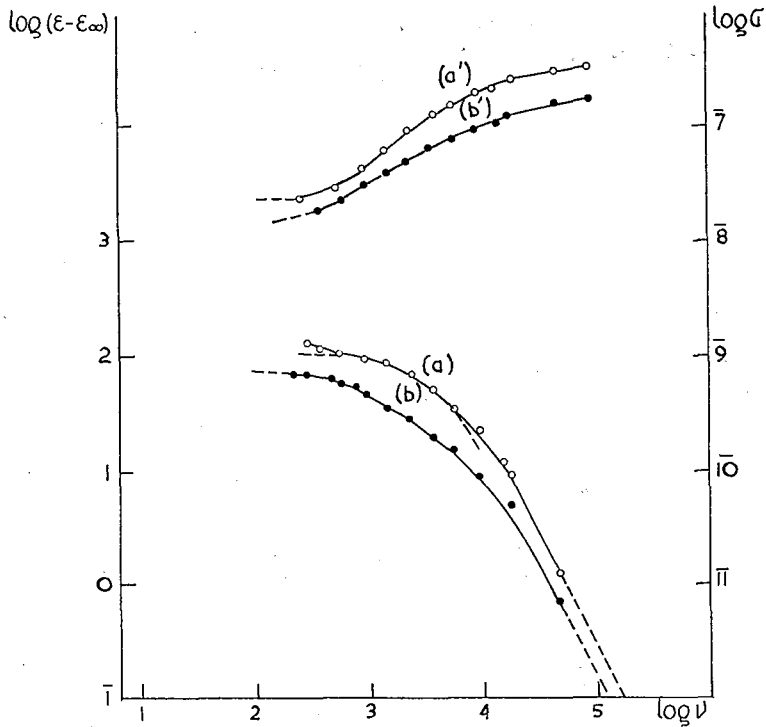


Fig. 3. Ice doped with  $\text{NH}_3$ ,  $C=5 \times 10^{-4}$  N. Curves (a) and (b), dielectric constant and curves (a') and (b'), conductivity at  $-10$  and  $-25^\circ\text{C}$ , respectively

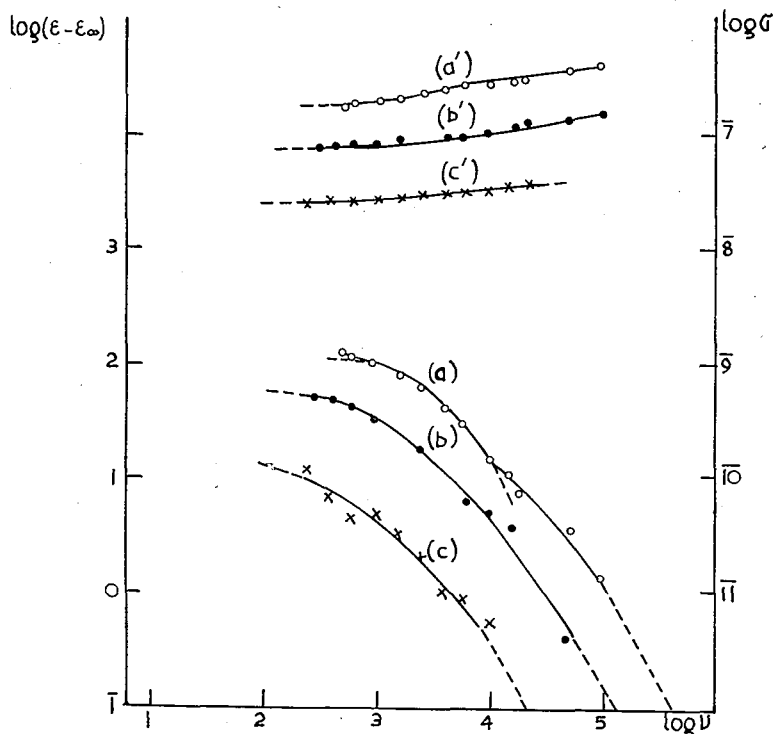


Fig. 4. Ice doped with  $\text{NH}_3$ ,  $C=6 \times 10^{-2} \text{ N}$ . Curves (a), (b) and (c), dielectric constant and curves (a'), (b') and (c'), conductivity at  $-10$ ,  $-25$  and  $-40^\circ\text{C}$ , respectively

Figure 1, curve (2) shows the logarithmic curve of the DC conductivity, as a function of the concentration, obtained at  $t = -10^\circ\text{C}$ . The general behaviour is similar to that observed for ice doped with hydracids, though the values of conductivity are lower and the inflection of the curve, at a concentration near  $10^{-3} \text{ N}$ , is more obvious than that of curve (1). Actually the conductivity attains at this concentration a value of about  $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$  and then remains constant for a further increase of the concentration.

In the concentrations  $C < 10^{-3} \text{ N}$ , the eq. (5) may be applied with  $r = 8 \times 10^{-17} \text{ ohm}^{-1} \text{ cm}^{1/2}$ . It must be noted that the conductivity is about two orders of magnitude lower than that of ice doped with hydracides in the same concentrations.

The frequency dependencies of the dielectric constant and conductivity for ice samples doped with different concentrations of  $\text{NH}_3$  are shown in Figs. 2 to 4. In each figure, curves a, b, c, and a', b', c', represent the real dielectric constant  $(\epsilon(\omega) - \epsilon_\infty)$ , and conductivity  $\sigma(\omega)$  measured as a function of the frequency, at different temperatures ( $-10$ ,  $-25$  and  $-40^\circ\text{C}$ ). It may be noted that at  $t = -10^\circ\text{C}$ , the curves of the dielectric constant nearly coincide with that of pure ice (Figs. 2 to 4). For all the concentrations the static dielectric constant is  $\epsilon_s = 100$  and the main inflection may be seen near the Debye frequency,  $\nu_D = 4 \times 10^3 \text{ c/sec}$ . However, for concentrations  $C > 10^{-4} \text{ N}$ , some divergence from the Debye dispersion is observed, marked by a secondary inflection at about  $10^4 \text{ c/sec}$  (curves (a) in Figs. 3 and 4). This divergence increases with the decreasing temperature. At  $t = -25^\circ\text{C}$  and  $C \geq 10^{-4} \text{ N}$ , the dielectric constant tends to a static value of about 50-

70 (curves (b) of Figs. 3 and 4); also the inflection near the Debye frequency is more indeterminate than in the pure ice, probably indicating the existence of more than one relaxation time. Finally, in curve (c) of Fig. 4, obtained at  $-40^{\circ}\text{C}$ , the slope of the curve changes slowly and the value of the dielectric constant at the Debye frequency for pure ice ( $\nu_D = 250$  c/sec) is still about 10, so that a static dielectric constant  $\epsilon_s = 20$  may be expected.

On the other hand, the average slope of the conductivity curves decreases with the increasing  $\text{NH}_3$  concentration, because the high frequency conductivity  $\sigma_{\infty}$  increases slower than the low frequency conductivity  $\sigma$  (which usually coincides with DC conductivity)\*; then  $\sigma_{\infty}/\sigma$  decreases with increasing concentration of  $\text{NH}_3$  though the difference  $\sigma_{\infty} - \sigma$  may be considered as nearly independent of the concentration. For  $C \geq 10^{-3}\text{N}$ ,  $\sigma$  and  $\sigma_{\infty}$  are of the same order of magnitude. Table 1 gives the average values of  $\sigma_{\infty}$ ,  $\sigma$ ,  $(\sigma_{\infty} - \sigma)/\sigma_{\infty}$  measured for different samples in concentrations  $\geq 10^{-3}\text{N}$ , and the corresponding values for pure ice.

Table 1.

	$t$ °C	$\sigma_{\infty}$ ohm $^{-1}$ .cm $^{-1}$	$\sigma$ ohm $^{-1}$ .cm $^{-1}$	$\sigma_{\infty} - \sigma$ ohm $^{-1}$ .cm $^{-1}$	$\frac{\sigma_{\infty} - \sigma}{\sigma_{\infty}}$
Doped ice	-10	$32 \times 10^{-8}$	$10 \times 10^{-8}$	$22 \times 10^{-8}$	0.68
	-25	$11 \times 10^{-8}$	$6 \times 10^{-8}$	$5 \times 10^{-8}$	0.45
	-40	$3.5 \times 10^{-8}$	$2.5 \times 10^{-8}$	$1 \times 10^{-8}$	0.28
Pure ice	-10	$20 \times 10^{-8}$	$0.1 \times 10^{-8}$	$20 \times 10^{-8}$	1
	-25	$5 \times 10^{-8}$	$0.03 \times 10^{-8}$	$5 \times 10^{-8}$	1
	-40	$1 \times 10^{-8}$	$0.007 \times 10^{-8}$	$1 \times 10^{-8}$	1

From this table an estimation of the activation energy of conductivity may be obtained; this is approximately  $E_a \cong 0.35$  eV, both for  $\sigma_{\infty}$  and  $\sigma$ . However a small difference between the activation energies of these conductivities is shown by the decrease of the ratio  $(\sigma_{\infty} - \sigma)/\sigma_{\infty}$  with the diminishing temperature and by the corresponding decrease of the static dielectric constant, observed previously. Actually, according to the theory (Jaccard, 1964),  $\epsilon_s$  may be expressed by

$$\epsilon_s = \frac{\alpha}{T} \frac{\sigma_{\infty} - \sigma}{\sigma_{\infty}}, \quad (6)$$

where  $\alpha$  is a constant and  $T$  the absolute temperature.

### c) Ice doped with HF and $\text{NH}_3$ in different ratios

The system ice+HF+ $\text{NH}_3$  was studied in DC at  $-17^{\circ}\text{C}$ . The results are given in curve (1) of Fig. 5. In this figure, the abscissa shows the logarithm of the concentration ratio  $[\text{HF}]/[\text{NH}_3]$  (where  $[\text{HF}]$  and  $[\text{NH}_3]$  are the concentrations of the corresponding electrolyte) and the ordinate the logarithm of the reduced conductivity  $\sigma/\sigma_0$ , where  $\sigma_0$  is the conductivity of pure ice ( $\sigma_0 = 5 \times 10^{-10}$  at  $-17^{\circ}\text{C}$ ).

\* The DC conductivity is indicated by  $\sigma$ , because  $\sigma_0$  will be used to indicate the DC conductivity of pure ice.



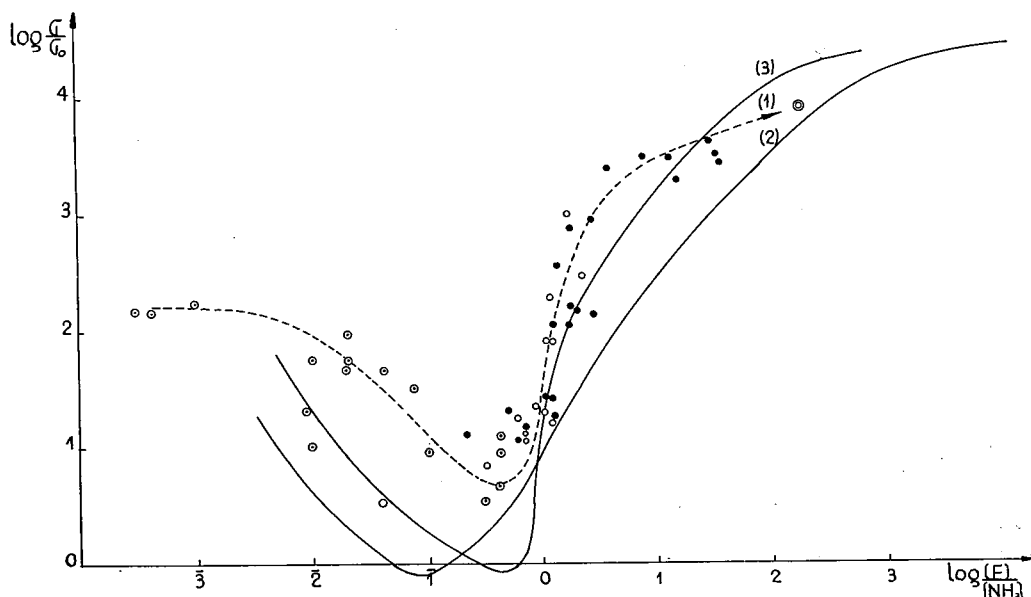


Fig. 5. DC conductivity of the system ice+HF+NH<sub>3</sub> as a function of concentration ratio; (1), experimental curve; (2) and (3), theoretical curves. Values of the constant in Table 4 was used for calculation of curve (3)

The results indicate (Levi, Milman and Suraski, 1963) that, in the range of  $10^{-2} \leq [\text{HF}]/[\text{NH}_3] \leq 5$ , the conductivity of the system may be considered as independent of the total concentration of the samples, being only a function of the concentration ratio. The graph shows two ascending branches, the conductivity increasing for F excess (right branch) and NH<sub>3</sub> excess (left branch). The latter was indicated by a dash line because the experimental results were more uncertain in this range, due to difficulties in the chemical analysis of the samples. The conductivity is particularly sensitive to small variations in the concentration around the equivalence point ( $[\text{HF}] = [\text{NH}_3]$ ), where  $\sigma/\sigma_0 \cong 50$ . The curve passes through a minimum for a small excess of NH<sub>3</sub>, where some samples show a conductivity relatively close to that of pure ice. For concentration ratios  $[\text{HF}]/[\text{NH}_3] \leq 10^{-2}$  or  $[\text{HF}]/[\text{NH}_3] \geq 10$ , the conductivity approximately coincides with that of ice doped with NH<sub>3</sub> or HF alone, in the same total concentrations.

A few experiments were also performed in AC on samples obtained from NH<sub>4</sub>F solutions, in high concentrations. In Table 2, the results obtained for  $C \sim 10^{-2} \text{ N}$  ( $-20^\circ\text{C}$ ) are compared with the corresponding ones for pure ice. The low frequency conductivity  $\sigma$  coincides with that of the equivalence point in DC, showing that  $[\text{NH}_3] = [\text{HF}]$ . Both

Table 2.

	$\sigma$ ohm <sup>-1</sup> cm <sup>-1</sup>	$\sigma_\infty$ ohm <sup>-1</sup> cm <sup>-1</sup>	$\epsilon$	$\nu_D$ c/sec
Doped ice	$1 \times 10^{-8}$	$5 \times 10^{-7}$	100	$8 \times 10^3$
Pure ice	$3 \times 10^{-10}$	$5 \times 10^{-8}$	100	$8 \times 10^2$

$\sigma$  and  $\nu_D$  (Debye frequency) are about one order of magnitude higher than for pure ice.

## DISCUSSION

According to the theory of the electric behaviour of ice (Jaccard, 1964), based on the mechanism of proton transfer, the AC and h.f. conductivities may be expressed as functions of partial specific conductivities  $\sigma_{\pm}$  and  $\sigma_{DL}$  of ionic and Bjerrum defects by the equations:

$$(e^*/\sigma) = (e_{\pm}^2/\sigma_{\pm}) + (e_{DL}^2/\sigma_{DL}) , \quad (7)$$

$$\sigma_{\infty} = \sigma_{\pm} + \sigma_{DL} , \quad (8)$$

where  $e_{\pm}$  and  $e_{DL}$  are the electric charge carried by defects,

$$e_{\pm} \sim e_{DL} \sim (e^*/2) , \quad (9)$$

and  $e^*$  is the proton charge.

For pure ice, it has been shown that  $(\sigma_{\infty}/\sigma) \sim (\sigma_{DL}/\sigma_{\pm}) \sim 10^2$  and eqs. (7) and (8) may be simplified by

$$\sigma = (e^*/e_{\pm}) \sigma_{\pm} , \quad (10)$$

$$\sigma_{\infty} = \sigma_{DL} . \quad (11)$$

The ratio  $\sigma_{\infty}/\sigma$  is generally reduced in doped ice. However, it has been shown that, with a few exceptions, the simplified expressions (10) and (11) may be applied, as a first approximation, in doped ice, so that  $\sigma$  and  $\sigma_{\infty}$  may be considered respectively proportional to the mobility and concentration of ions and Bjerrum defects.

a) *Dissociation of hydracids and NH<sub>3</sub> in ice*

According to the experimental results, it may be considered that the approximate expressions (10) and (11) are generally valid for ice doped with hydracids, in a wide range of concentrations and for ice doped with NH<sub>3</sub>, in concentrations  $C < 10^{-3}N$ . Thus, the proportionality between conductivity and the square root of concentration given by eq. (5) indicates that the electrolytes are dissociated according to the mass action law, and the constant  $\tau$  (which we will indicate by  $\tau_{HA}$  and  $\tau_{NH_3}$  for hydracids and NH<sub>3</sub>, respectively) is given by

$$\tau_{HA} = \mu_+ \sqrt{K_{HA}} , \quad (12)$$

$$\tau_{NH_3} = \mu_- \sqrt{K_{NH_3}} , \quad (13)$$

where  $\mu_+$ ,  $\mu_-$  are the mobility of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> ions and  $K_{HA}$ ,  $K_{NH_3}$ , the dissociation constants for hydracids and for NH<sub>3</sub>.

The estimated values of the dissociation constants  $K_{HA}$  and  $K_{NH_3}$  at  $-17^\circ\text{C}$  are given in Table 3. In this table, the computation of  $K_{HA}$  was made by the use of data of the proton mobility ( $\mu_+$

Table 3.

$\mu_+ + \mu_-$	$8 \times 10^{-2} \text{ cm}^2/\text{V. sec}$	} at $-17^\circ\text{C}$
$\mu_-/\mu_+$	1/10 .....	
$K_{HA}$	$3.6 \times 10^{-10} \dots 1.2 \times 10^{-9} \text{ mol/l}$	
$K_{NH_3}$	$3.8 \times 10^{-12} \dots 1.5 \times 10^{-13} \text{ mol/l}$	

+ $\mu_-$ ) obtained by Eigen De Maeyer and Spatz (1964) and of an estimated value of  $\mu_-/\mu_+$ , which ranges from 1/10 to 1. (The value of  $\mu_-/\mu_+$  will be discussed later). The value of  $K_{NH_3}$  at  $-17^\circ\text{C}$  was calculated taking into account the activation energy for dissociation  $E = 2E_a \sim 0.7 \text{ eV}$ .

On the other hand, the reduction in slope of the conductivity curves for a concentration between  $5 \times 10^{-2}$  and  $10^{-1}$  N, observed both for hydracids and for  $\text{NH}_3$ , suggests the existence of some effect limiting the number of charge carriers in ice. This phenomenon may be explained by Onsager's hypothesis (1960, 1962) that a fraction of ions formed by dissociation should combine with Bjerrum defects of the opposite sign, forming trapped ions which do not take part in the process of the electrical conduction. In these high concentrations, this effect may be important enough to reduce and eventually to stop the increase of the conductivity. However, one must not exclude the possibility of other effects that might reduce the increase of conductivity such as the formation of aggregates of impurity molecules in the solid or similar phenomena.

It may be shown that, if the observed effect is mainly due to the trapping effect, the equilibrium constants  $K_{\text{HL}_2}$  and  $K_{\text{OHD}_2}$  for dissociation of trapped ions in free ions and Bjerrum defects would coincide with the concentration of the electrolyte, in the region where the inflection of the conductivity curves is observed (Levi and Arias, 1964). However, if other phenomena were also important, these constants would be higher and we may put

$$\left. \begin{array}{l} K_{\text{HL}_2} \\ K_{\text{OHD}_2} \end{array} \right\} \geq 5 \times 10^{-4} \text{ mol/l} \quad (14)$$

It may be noted that according to these results, the fraction of trapped ions in pure ice would be negligible ( $\leq 1/100$  of the total ion concentration). On the other hand, if the upper limit in eq. (14) is considered, the values of dissociation constants which satisfy the experimental results would be about three times higher than the values given in Table 3.

b) *Ice doped with HF and  $\text{NH}_3$  in different ratios and dissociation constants involved*

Finally, the behaviour of electrolytes in ice crystals may be discussed taking into account the results obtained for the system ice +  $\text{NH}_3$  + HF, studied as a function of the concentration ratio of the electrolytes.

It may be easily shown, using the classic theory of electrolytes (Glasston, 1937), that the behaviour of such a system, treated as an electrolytic solution of a weak acid and a weak base, is in a qualitative agreement with the experimental results given by curve (1), Fig. 5 (Levi *et al.*, 1963). The higher dissociation of the hydracid with respect to the base, obtained by the separate study of ice doped with these electrolytes is confirmed by the following facts:

- 1) the slope of the conductivity curve is high in the region where  $[\text{HF}] > [\text{NH}_3]$ ;
- 2) the value of conductivity at the equivalence point is more than one order of magnitude higher than the conductivity of pure ice;
- 3) the position of the minimum of the curve, corresponds to a low excess of  $\text{NH}_3$  concentration.

According to the theory, the conductivity of the system depends on the concentration ratio  $[\text{HF}]/[\text{NH}_3]$  and on the parameters  $K_{\text{HF}}/K_{\text{NH}_3}$  and  $K_{\text{HF}}/\sqrt{K_0}$ , where  $\sqrt{K_0}$  is the concentration of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in pure ice. Curves (2) and (3)

Table 4.

	Curve (2)	Curve (3)
$K_{\text{HF}}/K_{\text{NH}_3}$	200	200
$K_{\text{HF}}/\sqrt{K_0}$	28	90

in Fig. 5 represent two theoretical approximations of curve (1), calculated for the values of the parameters given in Table 4.

On the other hand,  $K_{HF}(=K_{HA})$  and  $K_{NH_3}$  were obtained independently in Table 3. According to the most recent results (Eigen *et al.*, 1964),  $\sqrt{K_0}$  is

$$\sqrt{K_0} = 1.4 \times 10^{-10} \text{ mol/l at } -10^\circ\text{C} \quad (15)$$

The value of this constant at  $-17^\circ\text{C}$  may be calculated within an interval of uncertainty, due to the different values of the activation energy of pure ice conductivity, given by the bibliography. As the value of the activation energy varies from  $E=0.47$  eV (Eigen, De Maeyer and Spatz, 1964) to  $E=1$  eV (Heinmets and Blum, 1962), the value of  $\sqrt{K_0}$  at  $t=-17^\circ\text{C}$  may range between

$$8 \times 10^{-11} \leq \sqrt{K_0} \leq 4.6 \times 10^{-11} \quad (15')$$

Taking these results into account we obtain, at this temperature, the values of the parameters given in Table 5. In the first column they were calculated directly from Table 3, while in columns 2 and 3 the trapping effect was taken into account, with  $K_{HL_2} = K_{OHD_2} = 5 \times 10^{-4}$  mol/l. In column 3 the special values of the parameters which correspond to  $\mu_-/\mu_+ = 1/7$  were indicated. Here the uncertainty of the parameter  $K_{HF}/\sqrt{K_0}$  depends only on that of  $\sqrt{K_0}$  given by eq. (15').

Table 5.

	No trapping eff.	With trapping eff.	With trapping eff.
$\mu_-/\mu_+$	$10^{-1} \dots 1$	$10^{-1} \dots 1$	1/7
$K_{HF}/K_{NH_3}$	95 ... $8 \times 10^3$	95 ... $8 \times 10^3$	190
$K_{HF}/\sqrt{K_0}$	4.5 ... 26	13.5 ... 78	15 ... 26

Comparing Table 5 with Table 4, we observe that a good concordance is obtained for  $K_{HF}/K_{NH_3}$ , if we assume  $\mu_-/\mu_+ = 1/7$ . If the highest value of  $K_{HF}/\sqrt{K_0}$  in Table 5 is taken in these condition, both parameters approximate those of curve (2) in Fig. 5. A better approximation would be obtained if a higher value could be assigned to the last parameter, as it is shown by curve (3) in the same figure.

c) *AC measurements in ice doped with  $NH_3$  and dissociation constants of Bjerrum defects*

The DC behaviour of ice doped with  $NH_3$  has been interpreted in the previous paragraphs considering for all the concentrations,  $\sigma_{DL} > \sigma_{\pm}$ . The validity of this assumption is not immediately evident, but it results easily from the application of eqs. (6), (7) and (8) to the conditions  $\sigma_{\infty} > \sigma$  and  $\epsilon_s > 0$ , which are valid in all the studied range. On the other hand, the slow increase of  $\sigma_{\infty}$  with  $NH_3$  concentration shown in Figs. 2 to 4 indicates that the specific conductivity of Bjerrum defects  $\sigma_{DL}$  depends slightly on this concentration, *i.e.* that the dissociation constant  $K_{NH_3,D}$  corresponding to the process (4) is small. To obtain an estimation of this constant, we have applied eqs. (7) and (8) to calculate  $\sigma_{DL}$  for  $C \sim 10^{-3} N$ ; considering the concentration of L defects to be small with respect to that of D defects we may write

$$\sigma_D \sim \sigma_{DL} = e_{DL} \mu_D \sqrt{K_{NH_3,D} C} \quad (16)$$

The mobility  $\mu_D$  has not been evaluated directly, but all the results indicate that it is probably lower than  $\mu_L$  (Jaccard, 1959; Bryant and Fletcher, 1965). If we assume that

$$1/10\mu_L \leq \mu_D \leq \mu_L \quad (17)$$

we obtain

$$1 \times 10^{-4} \geq K_{NH_3,D} \geq 1 \times 10^{-6} \text{ mol/l} \quad (18)$$

These results may be compared with the behaviour in AC observed for ice doped with  $NH_4F$ . Zaromb and Brill (1956) and Camp (1963) have shown in their previous work that the relaxation time and the corresponding activation energy for ice doped with  $NH_4F$  are lower than for pure ice. This behaviour may be confirmed by the results given in Table 2. They show that, for  $C \sim 10^{-2} N$ , both  $\sigma_\infty$  and  $\nu_D$  increase by a factor 10 with respect to their value in pure ice. Since previous results indicate that L defects are completely dissociated from HF molecules in ice doped with  $NH_4F$ , process (2) must prevail with respect to process (4). Then, assuming the complete dissociation of L defects and the dissociation according to the mass action law for D defects, we obtain

$$C_L = \sqrt{\frac{K_{DL}}{K_{NH_3,D}}} \sqrt{C_{NH_4F}} \quad (19)$$

where  $C_L$  is the concentration of L defects and  $K_{DL}$  the product of equilibrium concentrations of D and L defects in ice. Considering the results in Table 2, we may put  $C_L \sim 10\sqrt{K_{DL}}$  for  $C_{NH_4F} \sim 10^{-2} N$  and replacing in eq. (19) we have

$$K_{NH_3,D} \sim C_{NH_4F} \times 10^{-2} \sim 10^{-4} \text{ mol/l} \quad (20)$$

If we compare eq. (20) with eq. (18) and we take into account previous results on L defect mobility, we finally have, for temperatures near  $-10^\circ C$ :

$$K_{NH_3,D} \sim 10^{-4} \text{ mol/l}; \quad \mu_D \sim (1/10), \quad \mu_L \sim 1 \times 10^{-5} \text{ cm}^2/\text{V. sec} \quad (21)$$

#### d) Conclusions

The results given in Table 5 and the comparison of eqs. (18) and (20) indicate that the electric behaviour of doped ice may be interpreted by the approximation that the processes (1) to (4) take place in the lattice. However, some discrepancy exists in the estimation of some parameters, as *e.g.*  $K_{HF}/\sqrt{K_0}$ ,  $K_{NH_3}/\sqrt{K_0}$ . Actually, if we attempt to completely justify the shape of the curve (1) in Fig. 5, these parameters should be about three times higher than those obtained from the experimental results.

At present there is not enough information to discuss the causes of this difference exhaustively. They could be at least partially related to the uncertainty of measurements in pure ice. Actually, it has been frequently observed that the complete elimination of impurities from distilled water is very difficult, and there is a possibility that the electric properties of ice may be modified by the existence of minute amounts of chemical impurities. In the most recent works on pure ice conductivity considerable care has been taken in the purification of water used in these experiments. However, the different values of activation energy obtained by different authors indicate that some errors could still exist in the results. On the other hand, the interpretation of the behaviour of doped

ice could be considered to be oversimplified. For instance, the hypothesis that the impurity molecules can incorporate substitutionally with H<sub>2</sub>O molecules in ice crystal lattice may be only partially correct. Actually, it would be difficult to apply it in a similar way to molecules similar in diameter to H<sub>2</sub>O molecules, as HF, and much bigger and of different features as HNO<sub>3</sub>. It may also be interesting to note in the present discussion that recent studies of diffusion in ice made by Camp (1963), Kopp, Barnaal and Lowe (1965), have shown that the diffusion coefficient of HF and NH<sub>4</sub>F are several orders higher than the coefficient of autodiffusion of H<sub>2</sub>O molecules; this could possibly indicate that interstitial molecules play some role in the observed phenomena.

Independently of these considerations, the results show that an asymmetry exists between the behaviour of ice doped with HF (or hydracids in general) and with NH<sub>3</sub>. This asymmetry is related to the different values of the dissociation constants and of the mobilities of similar defects of opposite sign.

It may be especially noted that the results given in eq. (21) support the hypothesis that  $\mu_D$  is lower than  $\mu_L$  and probably near to  $(1/10)\mu_L$ . A slightly higher value for this mobility has been obtained by Bryant and Fletcher (1965) who measured the thermoelectric effect in ice doped with HF and with NH<sub>3</sub>. They found  $\mu_D/\mu_L=1/2$ . At present, none of these results may be considered as completely reliable and similar causes of errors in the theoretical interpretation of the phenomena could be important in both cases.

Considering these different results we will state

$$(1/10)\mu_L \leq \mu_D \leq (1/2)\mu_L \quad (22)$$

On the other hand, theoretical calculations of the energy of formation of Bjerrum defects in pure ice show that a considerable distortion of the lattice must take place, specially around defects of the type D (Cohan *et al.*, 1962; Cohan and Weissmann, 1964). This would not probably be the case for L defects and could be a cause of the above asymmetry.

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