ELECTRICAL PROPERTIES OF SALINE ICE

by

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ABSTRACT

Electrical Properties of Saline Ice
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Results of a study of the complex dielectric coefficient, and related parameters of unidirectionally frozen artificial saline ice are given. Frequencies ranged from 20-Hz to 100-MHz. Salinities were of the order 4 - 20 ppt. Temperatures were varied from -35° to -15° C. An unusual cell which became incorporated into the ice as it grew is described and justification offered for its use.

Some of the results are analyzed in terms of a relaxation time distribution function obtained by numerical inversion of the pertinent relaxation integral equations in terms of the experimental data. Three different relaxation mechanisms are tentatively identified.
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PREFACE

In this thesis the following claims of original work are made:

1) Measurements, at various temperatures, upon individual samples of saline ice over a very wide frequency range (20-Hz to 100-MHz). The effects of salinity and electrode spacing were also investigated.

2) The inversion, by numerical methods, of the two relevant integral equations in terms of the experimental data.

3) The tentative identification of three possible electrical mechanisms suggested by this analysis.
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CHAPTER 1  INTRODUCTION

1:1 Preliminary Remarks

When sea water freezes the resulting ice contains entrapped brine, and, for this reason, is a very different substance from pure ice. The presence of this brine has a profound effect upon all of the physical properties. The structure of sea ice is extremely inhomogeneous and varies with the thermal history of the sample and even with time. Therefore electrical measurements, of a type which might be relatively simple with many substances, present an unusual challenge in the case of saline ice.

At the commencement of this study, little electrical data appeared to be available. General considerations of radio propagation in the Arctic, emphasized by more recent interest in the application of RF radio sounding techniques to an ice cover (Evans, 1961; Bogorodskii, 1963), indicated the need for a greater understanding of this subject.

For these reasons the present investigation was undertaken.
1.2 Saline Ice

Natural sea water usually contains about 3.5% by weight of dissolved inorganic salts. (This is usually expressed in terms of "salinity": (approximately) the number of grams of dissolved salts in 1000 grams of brine, in parts per thousand (ppt).) The principle ions present are Cl (19 ppt), Na (11 ppt), sulphate (2.6 ppt) and Mg (1.3 ppt). Many other ions are present in smaller quantities (Sverdrup, 1942).

Sea ice is formed when natural sea water freezes downward by one-dimensional cooling.

It is generally assumed that the actual ice produced during freezing is pure, with the dissolved salts being rejected by the ice. A fraction of these is entrapped within the ice forming pockets of relatively concentrated brine. The resulting structure has been frequently described (e.g. Pounder, 1963; Pounder, 1965; and Assur, 1958). The last author also gives a probable scheme of phase relationships between the components at different temperatures which was based upon the results of various chemical analyses. These matters have been recently reviewed by Weeks and Assur (1967).

Sea water commences freezing at temperatures somewhat below -1°C. The entrapped brine increases in
concentration as additional water freezes out until, around $-8.2^\circ C$, solid sodium sulphate decahydrate starts to precipitate. With further decrease in temperature the brine continues to become more concentrated. Near $-23^\circ C$ the deposition of solid sodium chloride dihydrate commences. On further cooling the relative amount of sodium ion decreases and at temperatures below $-35^\circ C$ other solid salts appear. It is generally thought that liquid brine still exists at temperatures below $-50^\circ C$.

The volume of liquid in the ice ("relative brine volume") has been calculated by Assur (1958) and is discussed in section 4:2. This quantity shows a relatively rapid change near $-23^\circ C$, the temperature of NaCl deposition. Natural sea ice shows salinities which range from less than 4 ppt for older ice to about 20 ppt for rapidly frozen new ice. Thus, not all of the salts in the original brine are entrapped, a sizeable fraction being rejected into the water underneath.

Ice forms hexagonal crystals which are uniaxially birefringent and thus the orientation of the single optic axis (c-axis) may be readily observed with crossed polaroids.

As sea-water begins to freeze, small thin discoids are formed near the surface (frazil ice). These float
on the water with a vertical c-axis orientation. As more discoids are formed they are compacted by the movement of the water and eventually freeze together into a solid cover. This is composed of small crystals of more or less random orientations, along with entrapped brine. Since growth of an ice crystal appears to be favoured along directions perpendicular to the c-axis, a selective growth process then takes place. Crystals which have their optical axes perpendicular to the temperature gradient grow at the expense of those less favourably oriented. This produces a transition layer below which the crystals generally show a horizontal c-axis orientation and grow in the form of vertical columns. The latter structure is usually established within a range of 5 to 20 cm below the surface.

It is important to qualify the use of the word "crystal" in this context. The term is applied to regions which were originally built up from thin (0.5 mm) parallel platelets of pure ice, separated by thin brine layers. As the freezing proceeded, ice bridges were formed between the platelets leaving the brine entrapped in long, thin, often parallel inclusions lying in regular rows along the sites of the original brine layers. "Crystal" therefore refers to a region within which all
of the ice has a common c-axis orientation, but which is traversed by rows of fine brine cells. Such regions are also referred to as "zones, "crystalloids", or "grains".

The crystal zones take the form of vertically elongated columns of irregular cross-section. The effective diameters are often of the order of several cm and increase with depth below the surface. The spacing between the rows of inclusions is often of the order of 0.5 mm and has also been observed to increase slowly with depth. The brine pockets, themselves, are commonly considered to be idealized cylinders of elliptical cross-section. The length of the inclusions is quite variable. They have been observed to extend for 2 or 3 cm. Their orientation is usually vertical. The diameters of these pockets are estimated to be roughly of the order of 0.05 mm, and depend on temperature.

The configuration of the brine is not completely fixed. When a temperature gradient is present, cells migrate slowly towards warmer regions. Furthermore, since there is some interconnection of the brine pockets, especially at warmer temperatures, some drainage of the brine may occur.

Brine is often also found at the grain boundaries.
The physical properties of a single zone are usually highly anisotropic when directions parallel to and perpendicular to the brine cell axes are considered.

1:3 Background

The electrical properties of pure ice, at temperatures above \(-40^\circ C\), are quite well established. Granicher (1963) and Hasted (1961) have reviewed most aspects of the subject. Jaccard (1959) and Dougherty (1965) have given theoretical treatments. Pure ice is considered, with appropriate references, in section 4:2.

When impurities are introduced into the system, the situation becomes more complex and less well understood. The simplest case involves the few ions or groups which are thought to fit substitutionally into the ice lattice. Possibly fluoride and ammonium ions are the only ones. Zaromb and Brill (1956) studied the case of \(\text{NH}_4\text{F}\) and showed that this substance forms mixed crystals with ice up to a certain concentration when a platelet structure became apparent. The presence of either of these ions in ice has a pronounced effect on the dielectric properties. They play a role somewhat analogous to that of doping agents in semiconductors (Granicher, 1963; Granicher et al, 1957; Dengel et al,
1966; and Arias et al, 1966). These phenomena are reasonably well understood. The effect of these particular impurities upon the dc conductivity has also been extensively studied (e.g. Levi et al, 1963).

However, when the ice system contains other impurity ions the situation is much less clear. A few authors who (sometimes more or less incidentally) have observed the dielectric properties of ice containing electrolytic impurities are: Smythe and Hitchcock, 1932 (from dilute KCl solutions); Workman and Drost-Hansen, 1954 (CsF); Yosida and colleagues, 1958 (snow of various degrees of purity); and Watt and Maxwell, 1960 (snow and glacial ice). These authors agree that the presence of even a small amount of impurity in an ice system has a pronounced effect upon the electrical properties. Both the real and imaginary parts of the dielectric coefficient are considerably increased. The dc conductivity of ice from dilute solutions of inorganic acids and alkali halides has been studied by Iribarne et al (1961).

Some authors have claimed to observe differences in the dc conductivity of impure ice upon reversal of current direction. Ostrem (1967) has noted this in a study of glacier ice and it has also been mentioned by
Truby (1953). The effect seems to be neither established nor understood.

A study of ice prepared from NaCl solutions led Workman and Reynolds (1950) to suggest the possible inclusion of some chloride ion into the ice structure. Subsequent work by Lodge et al (1956) indicated that both the sodium and the chloride ions were rejected by the ice at low freezing rates. This assumption is made throughout the present work, although the question of chloride inclusion has been tentatively put forth once more by Iribarne et al (1961) in connection with their electrical measurements.

Little work appears to have been done on the properties of sea or saline ice before 1960. Diichtel and Lundquist (1951) measured the electrical resistivity at various temperatures in both horizontal and vertical directions, obtaining higher values in the former case than in the latter. Do measurements are also reported by Pounder and Little (1959). Literature searches by Horigan (1953), Cook (1960) and this laboratory yielded little other information.

Cook (1960) performed a few experiments upon artificial ice at 100-MHz only. Bogorodskii (1963), and Bogorodskii and Rudakov (1963) published data obtained
with artificial ice over a limited range of radio frequencies. In 1964 Wentworth and Cohn reported a laboratory investigation of natural sea ice between 100-KHz and 30-MHz.

Some results of the present study have already been presented (Addison and Pounder, 1966) and, simultaneously, Fujino (1966) reported audio frequency measurements on natural sea ice. Some completely unspecified measurements above 100-MHz are reported by Ragle et al (1964), and low frequency, in situ, measurements on sea ice are referred to by Fujino (1966).

1.4 The Present Study

In this work a detailed study of the electrical properties of artificial saline ice was carried out at -22°C over a frequency range from 20-Hz to 100-MHz.

The study was then extended to include a range of temperatures from -35°C to -12.5°C. The effect of salinity was also investigated for salinities ranging from about 4 to 20 ppt.

An analysis of some of these results in terms of existing polarization theories is presented and three electrical mechanisms tentatively identified.
CHAPTER 2 EXPERIMENTAL PROCEDURES

2.1 Preparation of the Ice

The complexity of the electrical instrumentation required, and the difficulty of its use under Arctic conditions, indicated a laboratory project. Sea ice transported from the North is usually packed in dry ice and arrives with a complex thermal history. Furthermore, ice cores, originally taken vertically, usually must be stored in a horizontal position for long periods of time causing an uncertainty in the disposition of the brine. As a consequence, it was decided to study artificial saline ice, grown in the laboratory.

Previous studies (Perey and Pounder, 1958; Smith and Pounder, 1960) show similarities and differences between artificial ice and natural sea ice. The former, in many ways, resembles a scale model of the latter. The transition region is found about 1 cm under the surface, below which the crystalline zones tend strongly towards horizontal orientation of the c-axes. However, the grains in this case are generally smaller and less regular, being at most a centimeter or so in diameter. Grain length in artificial ice is generally found to be at most 7 or 8 cm, with many zones extending for only one or two centimeters. Also, the degree of parallelism between
the grains is not as high as is often noted in natural sea ice, and the structure is, in general, somewhat more chaotic.

It is to be expected that these differences would be reflected in the electrical measurements. The study should, nevertheless, provide information useful in the consideration of natural sea ice, as well as a possibility of identifying the electrical mechanisms present.

About 30 liters of brine were frozen in a deep vessel some 30 cm in diameter. The top was shielded but indirectly open to the air, and the brine level lay about 25 cm below it. All other surfaces were insulated with at least 30 cm of cork to approximate one-dimensional cooling. Small weighted air bladders were included to relieve pressure during freezing.

Examination of thin sections of this ice (under crossed polaroids) showed some tendency for grains to commence growing outwards from the side of the vessel for short distances before curving downwards. However, there was always an upper central region in the ice where the grain structure was vertical and approximated that of sea ice. While the salinity increased with depth, as salts rejected during freezing enriched the underlying brine, this structure was maintained down to about 20 cm
below the surface. Lower than this the grains became fragmentary. Therefore each mass of ice prepared could be relied upon to yield only a small cylindrical volume, about 15 cm long and 12 cm in diameter, which was considered suitable for study.

Artificial brine was prepared in accordance with a formula of Lyman and Fleming (Sverdrup, 1942) and contained all of the most significant ions present in natural sea water. The brine salinity was 35 ppt in all cases except one. There it was reduced by a factor of three to obtain lower salinity ice.

About 6 to 8 weeks were required to complete the freezing process. All brine was frozen in a cold-room at an ambient air temperature of -22°C.

2.2 Sample Format

Because of the large scale inhomogeneities of its multiple phase structure, saline ice presents uncommon problems in the selection of a sample format. To obtain measurements in any way representative of the bulk properties of the material, the sample cross-section area must be large enough to include several grains. When any piece of ice is cut from a larger mass, because of interconnection between the brine inclusions, it is well
Cook (1960) does report measurements based on brine frozen rapidly in a test-cell with dry ice. While perhaps adequate for his immediate purpose the samples cannot be considered to be at all representative of the sea ice structure. He reports other data for vertically cut slabs, but only at temperatures below -30°C, where brine drainage would be less significant.

Wentworth and Cohn (1964), on the other hand, apparently ignored this aspect and studied cylindrical discs of natural sea ice about 7 cm in diameter which were only some 3 mm thick. (They used a parallel plate cell with guard rings.) Since most of the brine inclusions would pass right through their specimens, the degree of liquid shift must have been large. Certain marked and curious anomalies in their results at higher salinities can probably only be explained (section 3:2) in terms of this.

Bogorodskii, at least in the references cited, says little about how the quoted values were obtained.

In the present investigation, the size of sample to be studied was dictated by the amount of suitable ice available. Most samples, in either of two formats, were 7.6 cm (3 inches) in diameter with a thickness of about 2 cm (0.75 inches) to correspond to the spacing of standard two-pin General Radio
electrical connectors.

Initial attempts to measure discs machined from the ice, sandwiched in a conventional manner between gold electrodes, enjoyed little success. The observations depended inordinately upon the method used to shape the sample and upon the degree of finish obtained. Presumably this was because of disturbance of the brine or the creation of electrical paths along the outside. Very large changes with time were found so that it was impossible to carry out any meaningful sequence of measurements.

A rather different approach proved successful. An unusual cell (Figure 1) was built up from rings of 7.6 cm ID lucite tubing having 8 fine, gold-metallized, nylon meshes stretched across diabolical planes, with uniform separations of about 2 cm (0.75 inches). The entire cell was about 50 cm in height and had slots near the bottom to allow free circulation of the liquid. These units were mounted vertically in the brine so that, when the ice formed, the meshes would be located within the desired upper central region of the mass. The uppermost mesh lay somewhat more than a centimeter below the surface to avoid the transition layer.

During freezing, ice would grow slowly downwards,
CONTACT PLUG

MESH

CLAMP

FIG. I MESH CELL
gradually incorporating the cell. Apart from the truncation, along a circular arc, of zones near the cell walls, no effect on the average grain size or structure was ever observed. There was also no evidence of grains growing horizontally from the tubing; in fact, parallelism was often slightly improved by its presence.

As the crystal zones grew downwards right through the meshes, careful examination never showed them to be perturbed in any way. (Metal mesh was unsuitable in this respect.)

The mesh itself was actually nylon "bridal veil" with 3 mm openings. After vacuum evaporation of gold, the electrical resistance was negligible.

Polished copper clamps, each bearing a banana plug, were fitted around the cell in direct contact along the entire circumference of each mesh. The exterior fittings were carefully water-proofed with dissolved lucite before placing the cell into the brine. After freezing, the vessel was cut up, and the ice-filled cell was extracted and carefully cleaned. It was then mounted vertically for study.

There are several obvious advantages inherent in this cell. The dimensions of the seven samples it
includes are known without manipulating the ice itself in any way. Since the cell contains some additional 20 cm of ice below the region considered, the latter is quite well sealed-off and reasonable long-term stability (several weeks at -22°C) was achieved. (This would appear, at first glance, to have been at the cost of electrical orthodoxy.) Furthermore, by measuring between non-adjacent meshes, several layers could be measured in series, thus varying the effective electrode spacing.

When electrical measurements (usually involving adjacent meshes) were complete, the cells were then sectioned vertically to ensure that the meshes were free from distortion and to observe the structure briefly. Then the salinity of the ice in each section was determined by means of the Mohr titration.

Considerable efforts were applied to an investigation of any possible electrical irregularities which might have arisen from the use of mesh electrodes. Often several layers were measured in series and the observations compared with calculations based on their individual properties. The simplest possible calculation, based on a number of lossy capacitors in series, provided quite good agreement with the measured values. (Further remarks and a diagram are to be found in Appendix I.)
It would be reasonable to expect that effects such as excessive contact resistance would become evident with the variation of the effective electrode spacing. No evidence of this sort was found.

In addition a number of spot-checks at selected frequencies were carried out using ice discs encircled by lucite and sandwiched between solid gold electrodes. These discs were obtained by freezing lucite tubes, without meshes, into the ice in a similar manner. Sections were cut, with the lucite left in place, and were then faced on a lathe. This second sample format proved quite satisfactory for a few rapid measurements before deterioration through brine drainage.

The results using each of these sample types were entirely similar over the complete frequency range. Because of structural differences, there were wide variations among individual samples, but the scatter with each method was observed to be of the same degree and over the same ranges of values. As a result, for purposes of calculation, the mesh electrodes were, perhaps naively, simply treated as if they were solid metal and the effective area taken to be the cross-section area of the samples. Saline ice is a predominately lossy material, especially at low frequencies. One would not expect the mesh electrodes to be useful for lower loss
dielectrics and, thus, no attempt was made to study, for example, pure ice.

All results reported here were obtained with the mesh cells. (Guard rings were not employed.)

2:3 Electrical Methods

In view of the variations in structure which generally exist between different samples of saline ice one cannot consider unique electrical properties characteristic of the medium as a whole. Results correspond only to the particular sample with which they were obtained. Electrical equipment was therefore selected in terms of simplicity and rapidity of measurement, rather than high accuracy.

Four standard commercial (General Radio, "G.R.") bridges were used to cover the frequency range from 20-Hz to 150-KHz.

<table>
<thead>
<tr>
<th>Frequency Range</th>
<th>Bridge Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-Hz - 20-KHz</td>
<td>Type 1603-A (ZY)</td>
</tr>
<tr>
<td>40-KHz - 3-MHz</td>
<td>Type 916-AL</td>
</tr>
<tr>
<td>500-KHz - 60-MHz</td>
<td>Type 1606-A</td>
</tr>
<tr>
<td>41 MHz - 150-MHz</td>
<td>Type 1602-B (Admittance Meter)</td>
</tr>
</tbody>
</table>

For frequencies up to 20-KHz null detection was achieved by means of a filtered amplifier (G.R. type
1232-A). This unit was also used (broad band) followed by an active band-pass filter (Khron-Hite 310-AB) up to 100-KHz. At higher frequencies heterodyne detection was employed. Up to 30-MHz this amplifier was used in conjunction with a G.R. 1232-P1 RF mixer and a local oscillator, at IF's of 20 and 100-KHz. For measurements above 40-MHz a G.R. type DNT heterodyne system was employed. The IF was 30-MHz and a low-pass coaxial filter was inserted to eliminate difficulties which arise from harmonics at certain frequencies. In all cases it is considered that the null-detection systems were more than adequate in terms of both sensitivity and bandwidth. Oscillators were mostly of the G.R. "Unit" type.

Ac voltage as delivered to the bridges was monitored with a G.R. type 1803-B VTVM, except above 50-MHz, where a G.R. 1263-B power supply served this purpose. A Beckman Model 7370 CRU frequency counter was included in the systems at frequencies up to 10-MHz. Higher frequency oscillators were calibrated. G.R. type 874 coaxial hardware, attenuators, etc., were employed throughout. The application of this apparatus was entirely conventional and in accordance with the manufacturers' suggestions.

Experience has shown that high-quality apparatus,
placed inside the cold-room for extensive periods of
time, tends to deteriorate. Therefore, the electrical
equipment was kept at room temperature and was connected
to the sample by means of a 1.8 meter G.R. type 874 co-
axial air line. (No flexible lines were used.) This
line had an electrical length of about 1.9 meters, an
observed low frequency capacity of 132 \( \mu \)f, and a nom-
inal characteristic impedance, \( Z_0 \), of 50 ohms. The
unit was especially sealed to avoid condensation. A
special connector, with a built-in copper shorting slide,
was fitted to the 1606-A bridge so that it could be
attached directly to the line. With this bridge only,
the line length was increased by an additional 30 cm to
allow comfortable access. Other bridges were connected
to the line with coaxial elbows and adaptors where
necessary.

The sample and the line were connected by means of
a 2-jack device. This allowed variation of the jack
spacing in multiples of 0.75 inches. It was designed
to bring the characteristic line impedance as near to
the sample as possible.

Initially, data reduction at audio and low radio
frequencies was done in terms of a lumped constant, while
a Smith Chart was used at higher frequencies. The results
showed considerable scatter. An investigation of the line itself showed departures from both nominal impedance and "losslessness". Detailed open and shorted measurements were made for both lengths of line. This data was smoothed, fitted (in a piecewise fashion) to empirical functions and written into a computer program. The sample data was then reduced, by complex arithmetic, using the full transmission line equations (Johnson, 1950) with no simplifying assumptions. This program also included all manufacturers' suggested corrections for bridge residuals, etc., as well as the frequency calibration data. Scatter shown by data reduced in this manner was greatly diminished.

Voltage applied to the input terminals for the various bridges was kept to a minimum. Usual values were 0.1 or 0.2 V RMS and never more than 0.3 V.

2:4 Experimental Program and Assessment

The first phase of the study involved measurements at -22°C only. A number of extremely detailed curves were taken at (logarithmic) frequency intervals of 1.1 to 1.2. When it was established that no fine structure was apparent, the number of points was reduced by \( \frac{1}{3} \). Most of the spot measurements using solid
metal electrodes were carried out during this period.

Considerable work at this time was devoted to procedural checks. Several samples were measured at low frequencies under continuously applied power for 36 hours. Most of the readings stayed constant within 10% and many to better than 5%. No effects were noted during these measurements which could be attributed to electrical melting, even when the maximum applied voltage was increased by a factor of 5. Various groups of layers were measured in series and comparisons were even made between values taken with ascending and descending frequency.

Many of the detailed curves were repeated several times at various audio frequencies over periods as long as 3 weeks. Varying degrees of reproducibility were observed. One sample, measured 6 times in 3 weeks, did not vary by more than ±4%. By contrast another sample showed a 50% shift in 3 days. However, many of the curves were reproducible within from 5% to 7% over 10 days and very few altered by more than 20%. The relative magnitude of the variations were similar for both the real and the imaginary parts of the data. No trend whatever could be discerned in the time variation. Each sample behaved differently, and sometimes erratically, in this respect. Since the disposition of brine
in the ice was not static, this variation is understandable.

The cold-room temperature was stabilized to better than 0.5°C and oscillated over this range with a period of about 15 minutes. The ice in the cell, being surrounded by a lucite jacket was sufficiently isolated from this complication that no periodic fluctuations were observed in the measurements.

In the second phase, the effect of temperature was investigated. The samples, when first removed from the mass, were initially measured at -22°C. Then they were cooled to -35°C and allowed at least 72 hours to stabilize. Curves were obtained at -35°C, -33°C, -31°C, -29°C, -27°C, -25°C, -23°C, -22°C, -20°C, -17.5°C and -15°C. (At the last temperatures the appearance of the ice had begun to alter.) At least 36 hours were necessary for the samples to achieve stability in each case. The cells were cooled once again to -22°C and a final curve taken before the ice was sectioned and analyzed.

Where bridge ranges overlapped, the curves usually showed an agreement roughly consistent with the above scatter. For example, at frequencies about 1-MHz, figure 2 illustrates an example where agreement was relatively poor. (A curve could not always be completed
in a single session and the usual point of interruption was between the two RF bridges.)

All of the temperature studies involved ice which became progressively warmer. This was because such long periods were required for the ice to stabilize after the initial shift from \(-22^\circ\), that it was desirable for the samples to spend this time at the lowest temperature to minimize deterioration.

A total of 6 cells were used. However the full complement of samples was not often available, because of either brine leakage and corrosion at one of the clamps, or, occasionally, distortion of one of the meshes. The results reported here represent about 30 samples.

The final cell was frozen in brine of only about 10 ppt salinity. In this case additional measurements were made upon layers in series to ensure that the mesh format was still useful with the lower salinity ice. (The temperature range in this case extended from \(-33^\circ\) to \(-12.5^\circ\).)

At audio frequencies, values for the real part of the dielectric coefficient are observed to scatter about a smooth curve to within \(\pm 5\%\) or less. At low RF, scatter increases somewhat. By 1-MHz, the calculations necessitated by the air line begin to contribute to the
experimental uncertainty. Data taken with either of the RF bridges show an average scatter of about 10% up to 20-MHz, increasing to 20% by 50-MHz, as inadequacies in the measurement format become apparent. Above this frequency, data is less coherent, but still adequate to suggest the curve shape up to 100-MHz (but, generally not beyond). Data for the imaginary part of the dielectric coefficient generally showed less scatter.

It is difficult to calculate firm confidence limits for the data. Except at lowest frequencies, the major uncertainties arise in the data reduction and in the inadequacies of the general format at higher frequencies, rather than in the actual bridge measurements. It seems reasonable, however, to infer these limits from the scatter. Temperatures were measured to ± 0.2°C.

In all of the measurements the electric field was applied vertically, parallel to the direction of the ice growth.
CHAPTER 3 EXPERIMENTAL RESULTS

3:1 General Comments

Each sample was considered to be equivalent to a conductance, \( G(w) \), and a capacitance, \( C(w) \), in parallel, where \( w \) is the angular frequency. Then, treating each pair of meshes as a simple parallel plate capacitor, the measured admittance, \( Y \), may be written:

\[
Y = G + j\omega C = j\omega \varepsilon_0 \kappa^* \frac{A}{L}
\]

where \( \varepsilon_0 \) is the permittivity of free space (MKS), \( A \) and \( L \) are the cross-section area and electrode separation respectively, and

\[
\kappa^* = \kappa' - j\kappa''
\]

is the (normalized) complex dielectric coefficient.

The ac conductivity, \( \sigma \), may be expressed in terms of the loss factor, \( \kappa'' \):

\[
\sigma = \omega \varepsilon_0 \kappa''
\]

Here, following the previous practice of some authors, the parallel resistivity, \( \rho = 1/\sigma \), will be given. The loss angle and the loss tangent are defined by:
Figures 2 to 6 show the frequency dispersions for five different samples which are representative of the study as a whole. They had the following salinities:

- Sample 1: 8.15 ppt
- Sample 2: 18.5 ppt
- Sample 3: 5.12 ppt
- Sample 4: 12.5 ppt
- Sample 5: 15.8 ppt

Samples 1 and 2 were measured only at -22°C and are included here both to illustrate the experimental scatter and because they are discussed in a subsequent analysis. Sample 3 was taken from the cell frozen in less concentrated brine.

The frequency dispersions for all of the samples are relatively similar. High values of $k'$ and $k''$ are noted at low frequencies, often being of the order $10^5$ to $10^7$. In most cases the loss factors decrease almost linearly with frequency over most of the range, while $k''$, at low frequencies, usually falls somewhat more rapidly. Values of $k''$ are greater than those of $k'$ for frequencies up to at least 1-MHz. The loss tangents
FIG. 2
SAMPLE 1

-22°C

SALINITY 8.15%
FIG. 3
SAMPLE 2
-22° C
SALINITY 18.5%
FIG. 4a
SAMPLE 3
VARIOUS TEMPERATURES
SALINITY 5.12%
FIG. 4b
SAMPLE 3
CONT'D
FIG. 5a
SAMPLE 4
VARIOUS TEMPERATURES SALINITY 12.5%
FIG. 5 b
SAMPLE 4
CONT'D

FREQUENCY (HZ)
FIG. 6a
SAMPLE 5
VARIOUS TEMPERATURES
SALINITY 15.8%
FIG. 6b

SAMPLE 5
CONT'D

FREQUENCY (HZ)
are therefore considerably greater than unity, indicating that saline ice is a predominantly lossy material over audio and low radio frequencies.

In many of the curves for $k'$ a definite downward concavity is seen in the vicinity of 10-KHz to 100-KHz. For samples 1, 3 and 4, this is quite pronounced. It is vestigial for sample 2 and, in the case of sample 5, appears to be almost completely masked by the lower frequency effects. This feature also shows up in the lower temperature curves of $k''$ for sample 3. It indicates the presence of a relaxation mechanism (Chapter 4) which contributes strongly to the observations over the middle of the frequency range. Two maxima are observed in many of the loss tangent curves. The one at higher frequencies is associated with this process.

From the diagrams presented here it might be deduced that this downward concavity becomes less prominent as the salinity increases. Such a conclusion is, in the light of the complete study, only partially justified.

The resistivities decrease rather slowly with increasing frequency up to 10-MHz, where the variation becomes more rapid. The relative change in this parameter seems to be greater in the case of higher
salinity ice.

At frequencies above 1-MHz the curves for $k'$ usually become somewhat flatter. The loss factor curves in this region also generally show a less rapid rate of decrease. Above this frequency there are corresponding dips to be found in the loss tangent curves, many of which commence to rise again by 100-MHz.

Measurements at different temperatures upon samples 3, 4, and 5 are shown in figures 4 to 6. Some of this data has been replotted versus temperature and is shown in figures 7, 8, and 9 respectively.

It is readily apparent that the electrical properties depend strongly on temperature and that this dependence is most pronounced at lower frequencies.

The downward concavity of the $k'$ curves is more prominent at lower temperatures, as the masking effect of the low frequency processes diminishes. This is also reflected by the fact that the right hand maxima in the loss tangent curves become more pronounced. Both of these maxima shift to lower frequencies with decreasing temperatures. The magnitude of this effect is seen to be larger in the case of the lower frequency maximum. The net result is a complicated
FIG. 7 SAMPLE 3
TEMPERATURE VARIATION
FIG. 8 SAMPLE 4
TEMPERATURE VARIATION
FIG. 9
SAMPLE 5
TEMPERATURE VARIATION
series of cross-overs in the loss tangent curves below 10-kHz.

In figures 7 to 9 it is seen that $k''$, at the lowest frequencies, decreases markedly with temperature. The resistivity changes somewhat less drastically.

Between $-22^\circ\text{C}$ and $-24^\circ\text{C}$, near the NaCl deposition temperature, extremely rapid variations may be seen in both $k'$ and $\rho$. The curves of Fujino (1966), which cover a much wider temperature range, show cusps at this temperature. This type of abrupt change is perhaps indicated at $-23^\circ\text{C}$ by the data of figure 7. In figures 8 and 9, while the experimental points do suggest cusps, these are not firmly established, and the curves have been drawn in two possible ways.

The position of the cusp for any one sample seems to be independent of frequency. They lie at slightly different temperatures for different samples, but are all found between $-23^\circ\text{C}$ to $-24^\circ\text{C}$. This variation is not considered to be the result of inadequate temperature measurement. It is possibly related to the fact that the curves were taken at successively warmer temperatures.

In figure 11 the data at 20-Hz for these three
FIG. 10
VARIATION WITH SALINITY

RESISTIVITY (OHM-M)

LOSS TAN
samples are plotted against the normalized brine volume (Section 4:2) rather than temperature. The presence of abrupt changes in the curves is strongly suggested. In any case, it is clear that the low frequency electrical properties show a pronounced variation over that range of temperatures where the brine content is increasing rapidly.

The sense of the loss tangent variation with temperature is different at high and low frequencies. This arises from the relative shifts of the maxima in the curves of this parameter versus frequency.

An interesting side-light of this investigation is the evidence of changes caused by temperature cycling in some of the samples. Table 1 shows measurements made on sample 5 at -22°C. They were obtained, respectively: when the ice was first removed from the mass, during the normal sequence of measurements starting at -35°C, and, after the sample had been cooled once more to -22°C. Some marked differences may be seen. No immediate explanation is offered.

Figure 10 attempts to show the effect of salinity upon the electrical properties. The solid lines join
FIG. 11
VARIATION WITH (NORMALIZED)
BRINE VOLUME AT 20 Hz
points representing samples which all came from one particular cell, and perhaps show something of a trend. (No attempt has been made to fit a proper curve to the points.) The dotted lines are arbitrary extrapolations to the lower salinity region where the scatter is somewhat less. All of these values were obtained at -22°C. (Not all of the samples are represented on this graph. The ice in one cell was accidentally destroyed after measurements were complete, but before the salinities could be determined.)

Table 1

Effect of Temperature Cycling on the Electrical Properties at 20-Hz, Sample 5

<table>
<thead>
<tr>
<th>State</th>
<th>$k'$</th>
<th>Resistivity (ohm-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newly removed</td>
<td>$2.85 \times 10^5$</td>
<td>917</td>
</tr>
<tr>
<td>Normal sequence</td>
<td>$2.86 \times 10^5$</td>
<td>883</td>
</tr>
<tr>
<td>Cooled again</td>
<td>$4.58 \times 10^5$</td>
<td>661</td>
</tr>
</tbody>
</table>

There seems to be some tendency towards larger values of $k'$ and smaller resistivities at higher salinities, however, it is seen that the structural differences between the samples played a greater role in these measurements than did the salinity alone.
3.2 Comparison with Other Work

The results of the present study show a reasonably good agreement with the data available in the literature.

Sample 3 may be compared with work on ice of comparable salinity published by Wentworth and Cohn (1964) over a similar range of temperatures. Within the limited frequency span of their investigation (100-KHz to 30-MHz) they report values of $k'$ which are quite close to those of sample 3 at temperatures below -30°C. Near -15°C, although some of their curves are incomplete, it may be estimated that the results are lower than those of the present study by a factor of about 1.5. At 30-MHz they obtained values for $k'$ of about 5 to 8, in fair agreement with those of sample 3. (They also made measurements perpendicular to the growth direction, finding smaller values of $k'$ and a less pronounced dependence on temperature.)

Their loss tangent curves for warmer temperatures also show maxima at about 300-KHz. As in the present case, these appear at lower frequencies when the ice is colder. At higher temperatures the heights of these peaks are smaller than the present values by as much as
a factor of 10. However, near the bottom of the temperature range the agreement is much better.

Their results also show a dependence upon salinity which suffers from considerable scatter. Points at higher salinities seem to be split into two distinct branches.

For ice of 8 ppt salinity they observed a rather curious temperature variation for both $k'$ and the resistivity. As in the present case, the latter quantity drops with increasing temperature. However, near $-23^\circ C$ it suddenly rises in an abrupt peak and then drops once more. A corresponding dip is observed in the curve for $k'$. These two features are much more pronounced at lower frequencies.

Since they made their measurements at successively warmer temperatures, it seems reasonable to suggest that, as soon as their very thin samples reached the temperature range where the quantity of brine increases rapidly, a good part of it drained away. This would explain the above anomalies and also why the general agreement with the present study is worse at higher temperatures.

Fujino (1966) reports data for sea ice of about
13 ppt salinity, at frequencies ranging from 100-Hz to more than 10-KHz, over a very wide range of temperatures. In the region of the present study he obtained values of k' from $10^4$ to $10^6$. These may be compared with those of samples 4 and 5. His data for the resistivity show a dependence upon frequency comparable with that of the present case, and cover a similar range of magnitudes. However, at temperatures above -22°C, his curves for k' fall less rapidly with increasing frequency than is observed here. (Fujino also notes quite similar values obtained in a direction perpendicular to the ice growth.)

The limited data of Bogorodskii is roughly comparable with the present observations. At -26°C and 100-KHz he found a value of k' of about 70, falling to 6 at 20-MHz, the latter value somewhat less than reported here.

Cock's (1960) rough 100-MHz measurements showed resistivities of the order of 100 ohm-meters and k' of about 5 near -22°C. Measurements at this frequency by Ragle et al (1964) indicated a value of k' of only 3, as well as much smaller loss tangents than observed in the present study.
CHAPTER 4 ELECTRICAL RELAXATION IN SALINE ICE

4.1 The Relaxation Time Distribution Function, $G(t)$

When a material contains a single dipolar mechanism whose response to a voltage step function is a simple exponential decay with a single time constant, the real and imaginary parts of its dielectric coefficient, under sinusoidal excitation, follow the well-known Debye dispersion equations with a single relaxation time, $\tau_0$ (Frohlich, 1958).

\[
\kappa'(\omega) = \frac{(\kappa'_0 - \kappa'_\infty) + \kappa'_\infty}{1 + \omega^2 \tau_0^2} \tag{1}
\]

\[
\kappa''(\omega) = \frac{(\kappa'_0 - \kappa'_\infty) \omega \tau_0}{1 + \omega^2 \tau_0^2} \tag{2}
\]

Here $\kappa'_0$ is the low frequency limiting value and $\kappa'_\infty$ accounts for contributions from any other processes which are rapid and follow the field closely over frequencies where the $\omega$-dependent terms are significant.

If $\kappa''$ is plotted versus $\kappa'$ in this case (the well-known Cole-Cole (1941) plot) a semi-circular locus results. (A similar plot involving the related complex conductivities is also valid (Grant, 1958).)
In any case of relaxation in which a dc conductivity, \( \sigma \), also exists, the measured loss factor will include an additional term. Without a model for the process (or an assumption that a simple Debye expression is valid) this term cannot be separated from the relaxation losses (Cole, 1961) which will then be of the form:

\[
\left[ \frac{\varepsilon'' + \frac{\sigma}{\varepsilon_0 \omega}}{\varepsilon_0 \omega} \right]
\]

The frequency dependent portions of the simple Debye dispersion (1) and (2), may be represented by a resistor and a capacitor in series. The equivalent circuit for such a substance may also contain a conductance (from \( \sigma_0 \)) and a capacitance (from \( k_\infty \)) in parallel with this combination. (When warranted by numerical magnitudes, the latter two branches will sometimes tacitly be ignored.)

When the material involves a multiplicity of these simple processes, (or the equivalent) with a continuum of relaxation times, \( \tau \), and if their contributions may be linearly superposed, the equations are generalized:

\[
h''(\omega) = \int_0^{\infty} \frac{G(T) dT}{1 + \omega^2 \tau^2} + k_\infty \tag{3}
\]
Here $G(\tau)$ is the relaxation time distribution function (or "spectrum") and is normalized to yield the low frequency limiting value,

$$k''(w) = \int_0^\infty \frac{G(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2}$$

(4)

The constant, $k_\infty$, describes effects of any rapid phenomena not included in $G(\tau)$. Macdonald and Brachman (1956) have exhaustively and usefully examined the relationship between $k^\tau(w) - k_\infty$ and $G(\tau)$. They show that these quantities, generalized to a complex frequency, may be inter-related through iterated Laplace, or Stieltjes, transforms. They also point out that $k'(w) - k_\infty$ and $k''(w)$ deriving from a common $G(\tau)$ are mutually related through the Kronig-Kramers relationships. (This does not include any contribution to the measured loss factor from a conductivity term.) It is also shown that a physically realistic, positive, $G(\tau)$ may be represented by many different RC series combinations all connected in parallel.
flow until the voltage exceeds the decomposition potential of the dissolved substance (in this case of the order of a volt or more). Then ions begin to be discharged and larger currents commence. At lower voltages, the electrodes are "blocking" and (as discussed later) polarization builds up, but the dc conductivity is relatively small. The same effect has been observed (at less than 1 volt) for pure ice crystals with metal electrodes (see section 4:2:b). In the present case, as the applied RMS voltages were less than 300 mV, it seems unlikely that the observed loss factors would contain any appreciable component from this source. Note that the contribution to $k''$ from a process of relaxation time, $\tau_0$, at frequencies somewhat greater than given by $\omega \tau_0 = 1$, also falls off as $1/\omega$. (A definite distinction must be drawn between these measurements and the dc investigations of sea ice mentioned previously. There, voltages many times greater than the decomposition potentials were used, and the situation was entirely different.)

Fortunately, a check (of a sort) on this hypothesis is possible. Figure 3 shows that $k'$ for sample 2, at low frequencies, decreases very roughly as $1/\omega$. An enlarged portion of this curve is shown in figure 14. This sample may then be analyzed, at low frequencies,
in terms of a case cited in a table of integral transforms given by Macdonald and Brachman (1956) (ignoring $k_{\infty}'$).

Thus if,

$$k'(\omega) = \frac{R}{1 + \omega S} \sim \left(\frac{R}{S}\right) \frac{1}{\omega}$$

for $\omega S \gg 1$

then the corresponding $G(\tau)$ is:

$$G(\tau) = \frac{2}{\pi} \left(\frac{R}{S}\right) \left[ \frac{1}{1 + \left(\frac{\tau}{S}\right)^2} \right]$$

and

$$k''(\omega) = \frac{2}{\pi} \frac{\omega S R \ln(\omega S)}{[(\omega S)^2 - 1]}$$

$$\sim \frac{2}{\pi} \left(\frac{R}{S}\right) \frac{\ln(\omega S)}{\omega}$$

for $\omega S \gg 1$

To determine the fitting parameters, $R$ and $S$, one point each was taken from the experimental curves for $k'$ and $k''$. 
These latter quantities were then calculated from the equations and are shown (dotted lines) on figure 14. The resulting \( G(\tau) \) is plotted (smooth curve) on the bottom graph of figure 12. (As these authors point out, this \( G(\tau) \) must cut off below some small value of \( \tau \), causing departures from the above equations at higher frequencies. This does not affect the present argument but explains why the latter curve is incomplete.) Thus, for this case at least, within the obvious approximation, both of the observed low frequency coefficients may be adequately described by a pair of functions related through the Kronig-Kramers equations, without the introduction of a dc term. Such a term will not be considered further.

\( G(\tau) \) may be determined only over a limited range of \( \tau \) since \( k' \) and \( k'' \) are known over a definite range of frequency. Equations (3) and (4) then must be used in the form:

\[
\begin{align*}
\bar{k}'(\omega) &= \int_{\alpha}^{\beta} \frac{G(\tau) d\tau}{1 + \omega^2 \tau^2} + \bar{k}'(\omega) \\
\end{align*}
\]
\[ k''(\omega) = \int_{-\infty}^{\infty} \frac{g(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} \]

The upper limit, \( \beta \), represents that value of \( \tau \) above which a \( G(\tau) \) of any reasonable magnitude will not contribute significantly to the observations. (The contributions to \( k' \) and \( k'' \) when \( \omega \tau \gg 1 \) decrease as \( 1/\omega^2 \) and \( 1/\omega \) respectively.) The low frequency data for \( k'' \) will contain information, it must be assumed, up to, at the most, about \( \beta \approx 0.1 \) second. Processes with \( \tau \) shorter than the lower limit, \( \alpha \), are assumed to yield a constant contribution to \( k'' \) and will have little effect on \( k'' \). Since the highest frequency included in this analysis (because of scatter) is 50-MHz, \( \alpha \) would be expected to lie between \( 10^{-9} \) and \( 10^{-10} \) seconds.

The integral equations were inverted numerically with a computer by a Monte Carlo type of calculation developed for the purpose.

Observed experimental data were plotted on a large log-log scale and very carefully smoothed curves were drawn. Twenty pairs of values were taken from these curves between 20-Hz and 50-MHz.
The range of $\tau$ was divided logarithmically into 4 channels per decade and $G(\tau)$ was synthesized in the form of a histogram. Starting from zero, a lengthy process was carried out, adding and subtracting increments, one at a time, in the various channels. Channels were selected in pseudo-random order. Each attempt was tested by numerical integration and accepted only if it served to reduce the sum of the squares of percent deviations between the $k'$ and $k''$, so calculated, and the input data. Over a considerable period of time $G(\tau)$ was built up, the RMS percent deviation dropping towards a final asymptotic value which was less than 4%. After every few steps, the process was interrupted to allow $k''$ to be adjusted in terms of best fit of $k'$ at high frequencies.

As the machine time involved was large, especially for setting the operating conditions of the program and investigating reproducibility, the analysis was applied only to samples 1, 2 and 4. These histograms are shown in figures 12 and 13.

Such a process is statistical rather than determinative and care must be taken in interpretation of the results. These must be examined in the light of difficulties analogous to those experienced in nuclear physics.
FIG. 12
DISTRIBUTION FUNCTIONS,
G(T), AT -22°C
FIG. 13  
SAMPLE 4  
G(T) AT VARIOUS TEMPERATURES

-15°  
-22°  
-17.5°  
-23°  
-20°  
-25°
FIG. 14 SAMPLE 2
LOW FREQUENCY - 22° C
and there referred to as "resolution" and "counting statistics". For instance, since $G(\gamma)$ lies inside an integral sign, the process is insensitive to fine structure. A pronounced high value in one channel accompanied by adjacent low values will often arise through an initial statistical anomaly followed by later compensation. Thus, for example, the severe variation near $10^{-7}$ second for sample 2, figure 12, is disregarded, as is the structure often noted between $10^{-8}$ and $10^{-7}$ seconds. Observations concerning these calculations are based on experience gained in running the program under different operating conditions and may not necessarily all be inferred from the limited number of graphs presented here.

The range of $\gamma$ shown is greater than that previously indicated for purely operational reasons. The region which should be considered is indicated by a solid line and varies somewhat from sample to sample. Since the input data contained some vestigial contributions from processes outside this range, the inclusion of the dotted portions was found necessary to assure reproducibility of the central portion, and to assist convergence. Generation in these regions was highly unstable and the dotted portions are not meaningful.
Table 2 presents the final value of $k_\nu$ in each case. Although these should be regarded merely as fitting parameters of the process, it is encouraging that they lie roughly about the order of $k_\nu$ for pure ice (section 4:2:b) and the UHF values for saline ice of Ragle et al (1964). The table also shows the RMS percent deviations obtained. (When small systematic errors were deliberately introduced into the input data at various frequencies, the quality of the resulting fit rapidly became very poor.) It may also be noted that, for larger $\tau$, $G(\tau)$ obtained for sample 2 shows a reasonable similarity to the simple function previously discussed.

The information contained in figures 12 and 13 which is considered to be significant, may be listed as follows.

1) The existence and location of a large peak near $10^{-9}$ seconds which is responsible for the observed dispersion at high frequencies. A distinct shift is seen (figure 13) at temperatures near $-23^\circ C$. (While confidence is expressed in the position of this peak, for reasons involving program convergence rates, the relative heights of these particular peaks on different graphs should not be compared.)
### Table 2

**RMS % Deviation and \( k'_{\infty} \) for Various Samples**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature (^{\circ}\text{C})</th>
<th>RMS Dev. (%)</th>
<th>( k'_{\infty} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-22°</td>
<td>2.5</td>
<td>4.4</td>
</tr>
<tr>
<td>2</td>
<td>-22°</td>
<td>2.7</td>
<td>2.9</td>
</tr>
<tr>
<td>4</td>
<td>-15°</td>
<td>2.3</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>-17.5°</td>
<td>2.1</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>-20°</td>
<td>1.8</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>-22°</td>
<td>2.4</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>-23°</td>
<td>2.1</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>-25°</td>
<td>2.8</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>-27°</td>
<td>1.8</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>-29°</td>
<td>2.8</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>-31°</td>
<td>3.1</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>-33°</td>
<td>1.7</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>-35°</td>
<td>3.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>
2) A smaller hump between $10^{-4}$ and $10^{-6}$ seconds, which shifts towards shorter $\gamma$ at higher temperatures, and is associated with the downward concavity of $k'$ over the mid-frequency range, as well as the higher frequency peaks in the loss tangent curves.

3) A wide mass of rather indeterminate shape for larger $\gamma$, often commencing between $10^{-4}$ and $10^{-3}$ seconds; which accounts for the low frequency observations. The bulk of this mass shows some tendency to shift toward the right at lower temperatures, and to decrease in magnitude.

Other details appear with some regularity, but on the basis of the present evidence, are disregarded.

A few additional comments on the calculations are to be found in Appendix II.

4:2 Component Substances

Table 3 (from Assur, 1958) shows the fraction of total ice volume occupied by brine at the temperatures of this study, for the case of ice salinity of 1 ppt. The actual fractional brine volume is calculated by multiplying these figures times the measured salinity (ppt) of the ice in question. The remaining volume is occupied by ice, solid salts and, perhaps, air bubbles.
Table 3
Normalized Brine Volume at Various Temperatures

<table>
<thead>
<tr>
<th>°C</th>
<th>Fractional Brine Volume (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-12.5</td>
<td>4.68</td>
</tr>
<tr>
<td>-15</td>
<td>4.13</td>
</tr>
<tr>
<td>-17.5</td>
<td>3.72</td>
</tr>
<tr>
<td>-20</td>
<td>3.38</td>
</tr>
<tr>
<td>-22</td>
<td>3.14</td>
</tr>
<tr>
<td>-23</td>
<td>2.97</td>
</tr>
<tr>
<td>-25</td>
<td>1.76</td>
</tr>
<tr>
<td>-27</td>
<td>1.21</td>
</tr>
<tr>
<td>-29</td>
<td>0.97</td>
</tr>
<tr>
<td>-31</td>
<td>0.82</td>
</tr>
<tr>
<td>-33</td>
<td>0.73</td>
</tr>
<tr>
<td>-35</td>
<td>0.67</td>
</tr>
</tbody>
</table>

4:2:1 Liquid Brine

Assur (1958) also tabulates the relative quantities of the components which exist in equilibrium at various temperatures for a somewhat idealized sea ice model. At -22°C the concentrations in the brine of the three most abundant ions, Na, Cl and Mg, are about 3.5N, 4.6N and 0.9N respectively (assuming a density of 1.19 g/cc for
the brine). From $-22^\circ$ to $-12^\circ$ the principal change is an increase in the quantity of water present, these normalities being reduced by roughly 1.5. Below $-23^\circ$ both the quantity of water and the relative importance of Na diminish rapidly, other ions become relatively more important, and the complexity increases.

It is difficult to assess the electrical properties of the brine with any certainty since directly applicable data do not seem readily available. It will therefore be assumed that the brine is roughly describable, at $-22^\circ$C, as a 4N solution of NaCl (with dilution at higher temperatures). (In this section, unreferenced data is based on The International Critical Tables (1933) or the Handbook of Chemistry and Physics (1966).)

It will be subsequently necessary to make the very crude approximation that these two ions have equal mobilities, ion conductances and ionic diffusion coefficients (Glasstone, 1942). Within this approximation, the latter coefficient, D, will be similar to that for NaCl (Glasstone et al, 1941). Assuming that proportionality between D and T, the absolute temperature, is valid here, one arrives at a rough estimate:

$$D \sim 1.2 \times 10^{-5} \text{ cm}^2/\text{sec} \quad \text{at } -22^\circ\text{C}. $$
D for this brine will vary only slowly at higher temperatures, dilution acting in opposition to temperature.

The equivalent conductance of 4N NaCl at -22° may be roughly estimated from its value at 0°C by reducing it (exponentially) assuming a drop of 2% per degree (Glasstone, 1942). This yields a conductivity for the brine,

\[ \sigma_b \sim 0.08 \frac{\text{mho}}{\text{cm}} = 8.0 \frac{\text{mho}}{\text{m}} \text{ at } -22^\circ C. \]

Reduction in concentration and increase in equivalent conductance oppose and this quantity should also vary slowly with temperatures up to -12°C. The above value refers to the ac parameter measured at frequencies high enough to obviate electrode polarization and it is assumed valid over all but the lower end of the present frequency range. (Debye-Falkenhagen dispersion is not considered at this concentration.)

The dielectric coefficient, \( k'_b \), of the brine is estimated from the value of 50 for 4N NaCl at 21°C (Hasted, et al, 1948), allowing a 20% increase at -22°C by analogy with pure water (Hasted, 1961).

\[ k'_b \sim 60 \text{ at } -22^\circ C. \]

This value, which is also not very temperature sensitive,
should hold until very high frequencies when water undergoes a Debye dispersion with a relaxation time of around $10^{-10}$ sec. (estimated from extrapolation of Hasted's (1961) data, allowing for the effect of the salt (Hasted et al, 1948)).

At frequencies below the KHz range, ions begin to have a chance to follow the field significantly. For applied voltages below the decomposition potential, ions approaching an electrode are not discharged (blocking electrodes) and a space charge polarization is created. Macdonald (1953) has treated this theoretically for a solution between parallel planar blocking metal electrodes, of separation, L. He assumed the special case of equal ionic mobilities ($\mu$), diffusion coefficients (D) and number of ions per unit volume ($c_0$). It is shown that the parallel capacitance $C_p(w)$ and conductance $G_p(w)$ approximate a Debye dispersion.

$$C_p = \frac{c_0}{1 + w^2 \gamma_b^2} + C_\infty$$

$$G_p = \frac{G_\infty w^2 \gamma_b^2}{1 + w^2 \gamma_b^2}$$
where $C_{\infty}$ is the usual geometrical capacitance (corresponding to $k'_b$) and $C_{o}$ and $G_{\infty}$ are low and high frequency limiting values respectively.

Referring all $C$'s and $G$'s to an area of cross-section 1 cm$^2$, he obtains:

$$G_{\infty} = \frac{2 \mu e c_o}{L} = \frac{\sigma_b}{L} \quad \text{(CGS - esu)}$$

(Here $e$ is the electronic charge.)

$$C_{o} = \left(\frac{k'_b \mu e c_o}{8 \pi D}\right)^{\frac{1}{2}} = \frac{L}{4} \left(\frac{k'_b \sigma_b}{\pi D}\right)^{\frac{1}{2}} \quad \text{(CGS - esu)}$$

$$\tau_b = \frac{C_{o}}{G_{\infty}} = \frac{L}{4} \left(\frac{k'_b}{\pi D \sigma_b}\right)^{\frac{1}{2}} \quad \text{(CGS - esu)}$$

where $\tau_b$ is the associated relaxation time. This dispersion may be represented by a series combination of $C_{o}$ and $G_{\infty}$, in parallel with $C_{\infty}$, if the latter is significant. Note that, while $G_{\infty}$ has the usual length dependence, $C_{o}$ is independent of length, and $\tau_b$ is proportional to it.

For the idealized brine at -22°C this yields:
How well this theory agrees with experiment is debatable. Direct determination of the equivalent series parameters for solutions generally do show a frequency dependence at low frequencies (Jaffe and Rider, 1952 and references therein). However, a careful study by Grahame (1946), which included IN NaCl, showed no significant variation of these parameters down to below 100-Hz, leading him to suggest that the more usual observations arise from additional complications at ordinary metal electrodes, obviated in his case by use of a dynamic system. This is supported by the marked effect of different metals noted by Jaffe and Rider. The Macdonald equations applied to IN NaCl at room temperature yield values of \( C_0 \) which are 2 or 3 times greater than those found by Grahame, and they also imply a more severe concentration dependence than that actually observed. It is considered adequate, however, to describe the brine in terms of a series RC combination as computed from Macdonald's model. (A somewhat analogous theory has been formulated by Chang and Jaffe (1952).)
4.2: b Pure Ice Crystal

With the possible exception of frequencies below 50 Hz where an additional space charge effect is sometimes noted, the ac electrical properties of ice are described by a simple Debye dispersion (Aqty and Cole, 1952; Granicher et al., 1957). The relaxation time, $\tau_1$, is given by

$$\tau_1 = 5.3 \times 10^{-16} \exp\left(\frac{E_r}{k_B T}\right)$$

The activation energy, $E_r$, is 0.575 ev and $k_B$ is Boltzmann's constant. This parameter is shown by the upper line on figure 15.

$$\tau_1 \sim 1.8 \times 10^{-4} \text{ sec} \quad \text{at } -22^\circ C$$

For polycrystalline ice, Aqty and Cole observed a low frequency limiting value

$$k_{\nu_i} \sim 100 \quad \text{at } -22^\circ C$$

varying from about 102 at $-35^\circ C$ to 97 at $-12^\circ$. (With single crystals, Humbel, Jona and Scherrer (1953) noted a 15% directional anisotropy.) The high frequency limiting value, $k_{\nu_i}$, has been observed up to centimeter wavelengths (e.g. Lamb, 1946; Eder, 1947; Cummings, 1952)
FIG. 15 VARIATION OF ICE RELAXATION TIME WITH TEMPERATURE
and is generally taken (Granioher, 1963) to be:

\[ \kappa_\infty \sim 3.2 \quad \text{independent of temperature.} \]

This dispersion adequately describes the real part of the dielectric coefficient over the present frequency range and the imaginary part above approximately 1KHz. At lower frequencies, do conductivity must be included. It has been shown (Workman et al, 1954; Decroly, Granicher and Jaccard, 1957) that this conductivity is by proton transport. With metal electrodes, and voltages less than 1 volt, the electrodes are blocking and the conductivity drops markedly (Granicher et al, 1957; Granicher, 1958; Eigen and deMaeyer, 1958).

Jaccard (1959), obviating the blocking effect, reports do conductivities proportional to \( \exp \left( \frac{-E_o}{k_B T} \right) \) with \( E_o \) around 0.6 ev. (More recently higher activation energies have been obtained - for example, Eigen et al (1962), as reported by Granicher (1963); Heinmets and Blum, (1963) - and interpreted by the latter as related to higher purity and better techniques.) It is adequate here to quote Jaccard's values which range from 

\[ 5 \times 10^{-9} \text{ mho/m at } -35^\circ \text{ to } 10^{-7} \text{ at } -10^\circ, \text{ and show a value} \]

\[ \sigma_0 \sim 2 \times 10^{-8} \text{ mho/m at } -22^\circ C \]
A diagram of Granicher (1958) suggests that this value, even when blocking is present, may be reasonably applied at 20 Hz and above.

4:2:0 Other Components

Any effect of solid salts, air, etc. will not be considered. (Meakins (1961) has observed that inorganic hydrates do not often show relaxation dispersion.)

4:3 High Frequency Dispersion

It was shown by Maxwell (e.g. Von Hippel, 1954) that when the substance between two electrodes consists of parallel layers of materials with different electrical properties, the effective complex dielectric coefficient usually follows a Debye dispersion, with the loss factor perhaps augmented by a \( \frac{1}{w} \) term arising from dc conductivity. Wagner (1914) applied this idea to a dilute distribution of small non-interacting conductive spheres within a medium which (because of the complexity of Wagner's equation 40 in the general case) is usually considered to have no dc conductivity. Again, within an approximation (Van Beek, 1960), a simple Debye dispersion with a single relaxation results. With the same restrictions, Sillars (1937) extended this concept to an ideal
dielectric containing a dilute distribution of uniform conducting prolate ellipsoidal inclusions, of circular cross-section, aligned parallel to the field. The length to diameter ratio is expressed by the ratio of the semiaxes, $a/b$. Again the system follows a simple Debye dispersion. The resulting interfacial polarization and the relaxation time increase rapidly as $a/b$ becomes much greater than unity. Furthermore, when ellipsoids of random relative dimensions and random orientations are present, a spectrum of relaxation processes results. By far the strongest contributions arise from those inclusions which have a high $a/b$ ratio and which are aligned parallel to the field. Those which are less elongated and/or misaligned have much less effect.

A limited success has been achieved by various authors in the application of these theories to relatively low conductivity inclusions of water, semiconductors, etc. in various waxes and plastics (Van Beek, 1963; a review by Meakins, 1961).

Saline ice, with high conductivity inclusions, many of a length comparable to the electrode spacing, does not fulfill the assumptions of these theories at all well. Nonetheless, an attempt will be made to see whether the experimental results may be qualitatively interpreted in terms of this model. This necessitates
ignoring the dc conductivity of the ice crystal. Since Wagner's equation indicates that these effects should be seen at high frequencies, the value \( k_{\infty 1}^i \) is used for the ice.

For properly aligned, uniform spheroids Sillars' equations are:

\[
\begin{align*}
    k' &= k_\infty + \frac{k_{\infty i} N}{1 + \omega^2 \tau_s^2} \\
    k'' &= \frac{k_{\infty i} N \omega \tau_s}{1 + \omega^2 \tau_s^2} \\
    \tau_s &= \tau_0 \left[ \frac{k_{\infty i} (n-1) + k_b'}{\sigma_b} \right] \\
    N &= \beta \left[ \frac{n^2 k_{\infty i}}{k_{\infty i} (n-1) + k_b'} \right]
\end{align*}
\]

(MKS)

Where, in the present case, \( k_\infty^i \) will be roughly equal to \( k_{\infty 1}^i \).
Here, $n$ is a function of $a/b$, and has the values

\[
\begin{align*}
\text{a/b < 1} & \quad \text{(oblate)} & n & \sim 1 \\
a = b & \quad \text{(sphere)} & n & = 3 \\
a \gg b & \quad \text{(long prolate)} & n & \sim \frac{a^2}{b^2} \left[ \ln \left( \frac{a}{b} \right) - 1 \right]
\end{align*}
\]

and $q$ is that fraction of the total volume occupied by the spheroids. Wagner's theory of spherical inclusions is included in the above for $n = 3$. This case yields a relaxation time of $7.4 \times 10^{-11}$ seconds, too short to be observed here. However, it seems reasonable to interpret the peaks in $G(t)$ near $10^{-9}$ seconds in terms of Sillars' ellipsoids. For sample 4 (figure 13) this peak lies about $2.4 \times 10^{-9}$ seconds at temperatures above $-22^\circ C$ and about $1.3 \times 10^{-9}$ seconds at lower temperatures.

The former requires a value of $n$ of 660, corresponding to a length to diameter ratio $a/b$ of about 50. If, for $q$, one uses the fractional brine volume (about 0.04 for sample 4 at $-22^\circ C$), the calculated values of $k'$ and $k''$ are roughly 4 times too large at 50 MHz. Thus, in first approximation, if the ice is described in terms of an ideal Sillars' model, it behaves effectively as if \( \frac{1}{2} \) of its brine were in correctly oriented inclusions...
having a length to diameter ratio of 50. The factor of \( \frac{1}{2} \) is not troublesome since, with the somewhat small and disordered grain structure of the artificial ice, considerable brine must exist in pockets which are less elongated (for example at grain boundaries) or incorrectly oriented. These will make a much less significant contribution. If all of the brine is required to exist in pockets of 0.05 mm diameter (Pounder, 1965) this implies an average brine cell length of only a few mm, in poor agreement with the centimeter lengths observed in natural sea ice (Pounder, 1965; Langleben, 1967; personal communication). The largest values of \( \tau \) which seem to be associated with these peaks are about \( 10^{-7} \) seconds, and this requires a value of \( n \) of \( 2.85 \times 10^4 \) or a length to diameter ratio of about 400. For a 0.05 mm diameter brine cell, this would imply a length of 2 cm, which is roughly, the interelectrode spacing. Since such big values of \( n \) tend to produce very large contributions to \( k' \) and \( k'' \), the quantity of brine effectively acting in this manner would, according to the model, appear to be small. The quantitative application of Sillars' theory in this instance, is, of course, questionable. In addition, normal brine cells are usually considered to be elliptical rather than circular in cross-section (e.g. Weeks and Assur, 1967). For these
reasons, the qualitative agreement obtained is considered satisfactory.

At lower temperatures the peak in $G(\tau)$ occurs at a value of $\tau$ smaller by about $\frac{1}{2}$, implying that, as the sample warmed through the vicinity of the NaCl $\cdot 2H_2O$ deposition temperature, and the brine volume increased, the average effective length to diameter ratio also increased by about 1.4. This suggests breakdown of some barriers within the brine networks. Except for this fairly small change, the effect of temperature in this respect appears to be small.

The peaks in $G(\tau)$ for samples 1 and 2 (figure 12) are comparable, except that the peak for the latter lies at somewhat larger values of $\tau$, suggesting a larger length to diameter ratio for this particular sample.

It may be concluded that the high frequency dispersion can be interpreted in terms of a multiplicity of Maxwell-Wagner-Sillars phenomena. No serious suggestions about the ice structure should be inferred from this analysis.

4.4 Mid-Frequency Dispersion

The peak in $G(\tau)$ lying between $10^{-5}$ and $10^{-6}$ seconds for samples 1 and 2 (figure 12) is seen in the
case of sample 4 (figure 13) to show a definite shift towards shorter $\tau$ at higher temperatures. Vertical bars, showing the range of $\tau$ in which the peak might be expected to lie, are plotted versus $1/T$ semilogarithmically on the lower part of figure 15. A limited choice of straight lines may be drawn through these bars. The line of least slope corresponds to an activation energy, $E_\gamma$, of 0.58 ev. The steepest (dotted) line represents 0.66 ev. This just about establishes that these peaks in $G(\tau)$ arise from protonic relaxation in the ice crystal. Assuming the solid line to be "correct" it will be observed that, compared with the values of $\tau$ for pure ice, the present relaxation times are reduced by a factor of roughly 35.

No immediate explanation of this phenomena presents itself. Comparably reduced ice relaxation times have been observed in mixed crystals of flouride-doped ice (Granicher et al, 1957). (The original brine from which the present ice was produced did contain a minute amount of flouride.) However, ice containing sufficient flouride to account for this reduction, also shows a reduced activation energy of 0.23 ev, a value clearly incompatible with the present observations.
It is often considered (e.g. Kauzmann, 1942; Powles, 1953) that one may sometimes consider a microscopic relaxation time to be intrinsically associated with the transition rate of an individual microscopic dipolar mechanism in the absence of resultant polarization fields from the surrounding medium. From this a macroscopic (observable) relaxation time for the bulk material is then calculated. This is longer, usually by some multiplicative factor whose value depends on what expression is used to describe the local field acting on the microscopic dipolar mechanisms. Powles remarks that this tendency of the polarization to maintain itself after the field is withdrawn should be present to some extent. Perhaps it might be suggested that, in the present case, the local field is complicated by a significant additional component originating from the interfacial polarization of the brine cells. Since this component would follow the applied field closely at mid-frequencies, it seems possible that the net effect might be to shorten the observed macroscopic relaxation time for the medium without appreciably affecting the proton activation energy. Such a suggestion is purely speculative.
4:5 Low Frequency Dispersion

The high values of $k'$ and $k''$ observed at low frequencies must be associated with migration of ions within the brine. The effective low frequency real dielectric coefficient of brine in a channel a centimeter or so in length, according to Macdonald's theory, is enormous. However, it is readily seen to be difficult to account for the observed result in terms of a Maxwell-Wagner-Sillars type of analysis. The equations suggest long relaxation times, but, even for values of $n$ of order $10^4$, large values of polarization are not predicted.

As a most extreme case, one may have recourse to a variant of another simple, idealized model also proposed by Sillars (1937). Here all of the brine is considered to exist in identical parallel tubes in contact with an electrode at one end and stretching almost through the sample, being separated from the other electrode by only a thin film of ice. The rough low-frequency equivalent circuit of such inclusions would then be a conductance and capacitance in parallel (corresponding to $\sigma_{0i}$ and $k_{0i}$ of the ice) placed in series with a series RC combination (representing the $C_0$ and $G_\infty$ of Macdonald's theory). Even for this model, the predicted $k'$ and $k''$ are orders of magnitude too small,
unless the ice film is assumed to be unrealistically thin.

One is drawn to the apparently inescapable conclusion that the predominant contribution to the low frequency measurements arises from brine in continuous channels from one metal electrode to the other. However, if Macdonald's picture is to be accepted, three difficulties appear to arise from this explanation. Firstly, if these paths consist of straight regular channels, the low frequency capacity of the sample would be largely independent of length. This is not consistent with the observations (Appendix I). Secondly, $G(\tau)$ would show a large contribution around $10^{-3}$ seconds, and relatively little for larger $\tau$. Thirdly, at the lower end of the range, the ac conductivity of the ice should increase quite rapidly with frequency.

These objections become less serious if one considers the possibility of irregularities in the geometry of the brine channels. The simplest of these might be occasional constrictions in the brine paths, and possibly would not need to be of a very serious nature. In the artificial samples studied, with the relatively chaotic mosaic patterns, the brine linkages were undoubtedly complex and tortuous. Even in a near-ideal single zone
of natural sea ice the suggestion is not unreasonable, since all that would be required is the presence of a salt crystal partially blocking the channel, or a local variation in the eccentricity of the elliptical cross-section, or perhaps even a bend. (An idealized diagram of Weeks and Assur (1967, their figure 17) is consistent with this sort of speculation.)

To see the possible effect of such an irregularity, one may consider two simple brine cylinders connecting the electrodes, identical except for the presence of a constriction at the mid-point of one of them. In the limit of low frequencies they would achieve similar polarizations since, according to Macdonald's model, this is associated mainly with the accumulation of blocked ions near the electrodes. However, the presence of the constriction would greatly limit the ability of the second channel to follow higher frequency fields and it would thus show a longer relaxation time (or times). Furthermore, at frequencies much greater than \( w\tau \approx 1 \) for the constricted channel, polarization would very possibly also begin to build up at each side of the irregularity so that the two sections would polarize with a degree of independence. Under these circumstances, the equivalent circuit of the path would be something like two series
RC combinations linked by the higher (probably resistive) impedance of the constriction. Thus the effective series capacitance of the channel would be reduced by a factor of up to 2. If doubling the electrode spacing also implies doubling the average number of irregularities in a given path, then, at all frequencies above \( w \gamma = 1 \) the effective capacitance of such a channel would show a more usual dependence upon length. In the case of three times the normal electrode spacing, figure 16 of Appendix I shows clearly that the measured values do begin to show a trend towards the constant capacitance case at the lowest frequencies of the study. The presence of irregularities would create a wide spread of relaxation times with a short \( \tau \) limit around \( 10^{-3} \) seconds, corresponding to relatively regular channels. Many of the distribution functions shown in figures 12 and 13 show that whatever mechanisms are active at larger \( \tau \) do indeed appear to have such a limit between \( 10^{-3} \) and \( 10^{-4} \) seconds. (It might be mentioned that Iribarne et al (1961) in studying the voltage step-function response of ice frozen from dilute NaCl solutions, observed complex transients which were analyzed in terms of a range of decay constants of order \( 10^{-3} \) to \( 10^{-2} \) seconds and larger. This coincides, in several cases, with regions where the present \( G(\tau) \) show major contributions.)
At frequencies much above \( \omega \tau = 1 \) for a given channel, its contribution to the ac conductance of the sample will be constant at the maximum value. Thus, except at very low frequencies the previously mentioned strong frequency dependence of the sample conductivity will not be realized.

Additional circumstantial support may be derived from consideration of sample 2 (figures 3 and 12). One need only assume that it differs from samples 1 and 4 in having a greater number of less irregular brine channels connecting the electrodes, and many of the differences in its behaviour are explicable. For instance, its resistivity shows a greater frequency dependence than do those of the other two and its \( \Gamma(G) \) is larger with less relatively prominent features, for \( \tau \) greater than \( 10^{-5} \) seconds. (Perhaps this even may explain the fact that the Maxwell-Wagner-Sillars peak occurs at a larger value of \( \tau \), in accordance with a suggestion to be made subsequently.)

The observable results of a polarization phenomena involving irregularities in the paths should be, and are, temperature sensitive. Changes in irregularities should occur rapidly at temperatures near \(-23^\circ C\) and the measurements confirm this, especially at lower frequencies.
Figure 13 shows that the values of \( G(\tau) \) above the range \( 10^{-4} \) to \( 10^{-3} \) seconds diminish at low temperatures relative to other parts of the spectra. Some tendency toward shift of the stronger contributions to larger values of \( \tau \) is also indicated, all of which is consistent with an increasing degree of irregularity in the brine paths. It may also be observed that the low frequency dispersion of \( k' \) for sample 3 (figure 4) seems to be dropping out of the picture at lower temperatures leaving only the proton ice mechanism active at low frequencies. (A bulge corresponding to this ice dispersion is starting to appear in the \( k'' \) curves.) That this trend is real is clearly illustrated by the lower temperature measurements of Fujino (1966). Since appreciable liquid brine is still present in the ice it strongly suggests a closing off of the direct brine paths.

A conclusion inherent in this reasoning is that, if measurements were performed upon a sea ice slab which, because of extreme thickness (or accident) had no direct brine linkages between the electrodes, the large low frequency dispersion would not be seen, and the observed electrical properties below the KHz range would then be roughly similar to those of pure ice (within, say, a factor of 10).
The suggested partial "fragmentation" of electrical polarization at an irregularity in a channel, for frequencies higher than \( \omega \tau = 1 \), perhaps supplies a hint as to why, in the Maxwell-Wagner-Sillars dispersion the brine appears to act as if it were in shorter inclusions than would be expected.

4.6 In Conclusion

The purpose of this section has been to explain qualitatively the observed electrical properties in terms of three distinct mechanisms.

1) High frequencies: Maxwell-Wagner-Sillars dispersion.

2) Mid-frequencies: Debye dispersion of the ice protons with reduced relaxation time.

3) Low frequencies: dispersion resulting from ion-space-charge polarization in brine channels stretching between the electrodes.

It is hoped that these suggestions have been shown to be in accordance with the loose application of existing polarization theories to models which are not inconsistent with the accepted structure of saline ice. It must
be emphasized that there is implied no attempt to proceed in the reverse sense: that is, to claim that the electrical measurements have established any new or definite conclusions about the structure of the material.
APPENDIX I

EFFECT OF SAMPLE THICKNESS

A number of measurements were made by choosing mesh electrodes so that 2 or 3 layers were effectively placed in series. Their individual properties were first determined separately. Figure 16 shows typical results for the case of 3 layers. The points represent the measured values.

If one assumes the simplest model: that the combination may be represented by the independent properties of the layers, each denoted by a $G$ and $B$ in parallel, all connected in series, the equivalent properties of the combination are given by

$$\frac{k'' + j k'}{k'' + j k'} = \frac{M}{\sum_{i=1}^{M} \left( \frac{1}{k_i'' + j k_i'} \right)}$$

where $M$ is the number of layers. The graph shows that this agrees well with the observed values, especially in view of the fact that days sometimes elapsed between the pertinent sets of measurements. Various other arbitrary models were tried assuming contributions from contact resistance, but the agreement was never
FIG. 16
3 SAMPLES IN SERIES
-22°C

- MEASURED
- - - CALC: CONSTANT CAP.
- - - - - - CALC: SIMPLE SERIES
better than for this model.

An additional case, that of constant capacitance was tried, and is also shown on figure 16. Here when the properties of the individual layers were converted to series values for summation, it was assumed that the capacitance of the combination would be the same as the average capacitances of the component layers. With this assumption (taking the arithmetic mean of the individual series reactances, rather than capacitances, for simplicity,) we obtain

$$\begin{align*} k_{eq}'' + j k_{eq}' &= \frac{M}{\sum_{i=1}^{N} \text{Re}\left(\frac{1}{k_i'' + j k_i'}\right) + \frac{1}{M} \sum_{i=1}^{N} \text{Im}\left(\frac{1}{k_i'' + j k_i'}\right)} \end{align*}$$

This is seen to provide a poor fit for $k'$. However, as has been mentioned, the measured values do begin to depart from the first model towards this one at lowest frequencies.
APPENDIX II

ADDITIONAL NOTES ON THE MONTE CARLO CALCULATION

The relevant range of γ was split logarithmically into channels of equal width, the ith channel lying between $T_i$ and $T_i/\gamma$ where $\gamma$ is $\sqrt{10}$ and $m$ is the number of channels per decade. If the height of the ith rectangle in $G(\gamma)$ is $Y_i$, its contributions to the integrals (3) and (4) are, respectively:

$$\frac{Y_i}{w} \tan^{-1} \left[ \frac{wT_i(1-\frac{1}{\gamma})}{1 + \frac{w^2T_i^2}{\gamma}} \right]$$

and

$$\frac{Y_i}{2w} \ln \left[ \frac{\gamma^2w^2T_i^2 + \gamma^2}{w^2T_i^2 + \gamma^2} \right]$$

The integrations were performed by summing these terms over all channels. The $w$-dependent functions were calculated for all pertinent values of $w$, $\gamma$ and $T_i$, and were placed into core storage at the beginning of the program. Thus execution required only a summation of terms each obtained by a single multiplication.
In practice, to save time, the range of $\tau$ was divided initially into one channel per decade and $G(\tau)$ roughed-out (to an RMS % deviation of around 30%). Then using these results, the program switched over to 2 channels per decade until an RMS fit of 15% had been obtained and finally divided again, using 4 channels per decade to completion.

Much trial and error was carried out to ascertain the optimum range of $\tau$ to be employed. The main considerations were, firstly, that the shapes of the solid line portions of the spectra should not be altered by deliberate variations of the range. This was not true when it was too small. Secondly, the best possible fit was desired and, thirdly, it was necessary to have the range as small as possible to keep the number of channels to a minimum. At the earliest stage of execution a suitable positive or negative increment to $Y_1$ was found to be $10^7$, with some attempts using progressively smaller increments being made if this proved too large, before trying another channel. As the process converged, smaller and smaller initial increments (by as much as a factor of 30) were employed.

The running time was lengthy, requiring between 30 to 45 minutes for each run.
BIBLIOGRAPHY


Eder, F.X. (1947) Annalen der Physik (Folge 6) 1, 7-8, 381.


Glasstone, S. (1942) *An Introduction to Electrochemistry*, Van Nostrand, N.Y.


Meakins, R.J. (1961) Prog. in Dielectrics 3, 149.


Sverdrup, H.U. et al. (1942) *The Oceans*, Prentice Hall, N.Y.


Van Beek, L.K.H. (1963) in Magnetic and Electric Reso-

Von Hippel, A.R. (1954) Dielectrics and Waves, Wiley,
N.Y.


Watt, A.D. and Maxwell, E.L. (1960) J. Res. NBS, USA,
64D, 357.

Weeks, W. F. and Assur, A. (1967) The work cited was in
preprint form and is entitled "The Mechanical Prop-
erties of Sea Ice". It was issued by the U.S.
Army Cold Regions Research and Engineering Labor-
atory, Hanover, N.H., U.S.A.

Wentworth, F.L. and Cohn, M. (1964) J. Res. NBS, USA,
68D, 681.


