Thermodynamics of Irreversible Processes Applied to Ice

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With 1 Figure

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We consider only the four intrinsic electrically active defects with the highest mobility: the positive and negative ions (OH$^+$ and OH$^-$) and the valence or Bjerrum defects (vacant or doubly occupied hydrogen bonds). Assuming chemical equilibrium of the system, the entropy production is calculated in the linear approximation, especially the part of it resulting from changes of the proton configuration. The investigation of the electrical properties yields a Debye mechanism for the conductivity, and physical interpretations are found for the occurring phenomenological parameters. The anisotropy of the static dielectric constant is shown to be due to the anisotropy of the dynamical defect charges. Two characteristic times are found for the field relaxation, which are different of the Debye relaxation time. The electrostatic interaction between the defects is calculated for arbitrary concentrations. The electrochemical, mechanoelectrical and thermoelectrical effects are investigated, together with the inverse effects.

Ne considérant que les quatre défauts intrinsèques à grande mobilité: les ions positifs et négatifs (OH$^+$ et OH$^-$) et les défauts de valence ou de Bjerrum (valences hydrogène vides ou doublement occupées), admettant l'équilibre chimique, on calcule la production d'entropie en approximation linéaire, et spécialement la contribution des changements de la configuration des protons; l'étude des propriétés électriques livre un mécanisme de relaxation de Debye pour la conductivité, et on trouve une interprétation physique pour les différents paramètres phénoménologiques. L'anisotropie de la constante diélectrique statique est attribuée à celle des charges dynamiques des défauts. La relaxation du champ comporte deux temps caractéristiques, différents de celui de la relaxation de Debye. L'interaction électrostatique entre les défauts est calculée pour des concentrations arbitraires. L'étude s'étend aussi aux effets électrochimique, mécanoélectrique et thermoelectrique, ainsi qu'aux effets inverses.

1. Introduction

The importance of ice in nature and its peculiar physical properties have given rise to many investigations, which cover almost all the usual fields of physics. Among these, the question of the structure could be elucidated completely and the results can be found in recent publications \cite{7, 8, 16, 18}. Another field which aroused much interest is the electrical behavior of ice, characterized by a large dielectric constant, a polarisation relaxation of the Debye type \cite{1, 10} and a very low conductivity \cite{3, 5, 11, 13}. Moreover, the influence of certain chemical impurities, such as hydrofluoric acid, is very large \cite{18}, and these effects have been useful for the interpretation of the pure ice results \cite{17}. All these properties could be understood only with the hypothesis of mobile lattice defects, and an analysis \cite{7} of the possible mechanisms for all the known defect types leads to the conclusion that two classes, with each two defects of opposite charge, are necessary to explain the electrical behavior; they are the ions $\text{H}_2\text{O}^+$ and $\text{OH}^-$, and the Bjerrum valence defects \cite{2}, the bonds between two neighboring oxygen atoms containing two protons (D-defect) or no proton at all (L-defect), whereas the normal bonds have one proton. This hypothesis leads to several microscopic theories to explain the electric \cite{11, 15, 18} and later the thermoelectric properties \cite{12}. A review on this subject has been published recently \cite{9}.

These theories yielded quite satisfactory results, at least with respect to the understanding and interpretation of the phenomena; however, from the quantitative point of view, they were not able to bring light into every detail, because the knowledge of the basic microscopic models is still fragmentary. For example, the influences of the ions and of the valence defects on the thermoelectric properties are entailed with different numerical factors (29 and 32), although the roles of both defect classes in the lattice are perfectly symmetrical and complementary. Moreover, these factors are included in the formula relating the static dielectric constant with the defect charges, so that the determination of the latter from the experimental values of the former is subject to a possible uncertainty. A way of improving the theory would be to have better models, but these can evolve only from long and complicated quantumtheoretical calculations. Another way consists in looking at the problem from the phenomenological side, and to apply the thermodynamics of irreversible processes, which takes all the possible interactions between the defects automatically into account.

In this work, the general thermodynamic results \cite{4} will be applied, but in a somewhat different form. Instead of the mass currents (kg/m$^2$ sec) and mass forces (m/sec$^2$), the defect currents (number of defects/m$^2$sec) and forces (kg m/sec$^2$ per defect) will be considered. This transformation leaves the entropy production invariant, so that the Onsager reciprocity relations conserve their validity. It has also to be kept in mind that all the currents refer to the center of mass of the system; but as the number of moving protons in any process is quite negligible with respect to the total number of the molecules, the currents may as well be related to the lattice.

The purpose of this work is to calculate the entropy production, and, using the Onsager relations, to calculate the coefficients for the steady state effects relating the electric field and current to the concentration, pressure and temperature gradients, together with the treatment of certain time dependent phenomena.
2. Lattice and defects

We consider the hexagonal lattice, with the oxygen atoms in tetrahedral arrangement, at a distance \( r_{00} = 2.76 \, \text{Å} \) apart, disregarding the possible existence of oxygen vacancies, interstitial molecules and dislocations. Assuming that the tetrahedra are regular, there are then,

\[
N_0 = 3 \sqrt[3]{3/8} r_{00}^3
\]  

(2.1)

oxygen sites per unit volume. The oxygen atoms are linked by hydrogen bonds \( V \) governed by the Bernal-Fowler rules, which are: 1) there is one H-atom between two oxygen atoms, 2) two H-atoms are close to one oxygen atom (at a distance of 0.99 Å). The proton configuration is assumed to be at random within the limits of these rules. The only intrinsic defects that will be considered here are those produced by their violation, the doubly occupied and the empty bonds (D and L) and the positive and negative ions (\( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \)) which are produced in the following chemical reactions

\[
\text{H}_3\text{O}^+ + \text{OH}^- \rightleftharpoons 2 \text{H}_2\text{O}
\]  

(2.2)

and

\[
\text{D} + \text{L} \rightleftharpoons 2 \text{V}.
\]  

(2.3)

The presence of chemical impurities in the lattice is not excluded and they may give rise to reactions yielding any sort of defects. However, we assume that these chemical impurities are immobile so that they do not contribute to any irreversible process. This is true of course only in first approximation, but it is justified by the fact that their diffusion is many orders of magnitude smaller than for the intrinsic defects [14, 17]. On the other hand, the chemical equilibrium is established very rapidly [6]; as the processes considered here are either static or with much longer characteristic times, we assume that they occur in a situation of chemical equilibrium. Moreover, the latter should not be perturbed by the applied electric fields, so that effects pertaining to field dissociation or saturation are disregarded.

The indices 1, 2 will be attributed to the positive ions and the negative ions respectively, and the indices 3, 4 to the D and L-bonds respectively. We denote the absolute concentrations (m\(^{-3}\)) by \( n_i \) and by \( c_i \) the concentrations relative to the total number of molecules or bonds. The \( c_i \) are then subject to the relations

\[
\sum_i c_i (\text{ions, molecules}) = 1, \quad c(\text{H}_2\text{O}) \approx 1 \quad \text{and}
\]

\[
\sum_i c_i (\text{bonds}) = 1, \quad c(\text{V}) \approx 1.
\]  

(2.4)  

(2.5)

The regular molecules and bonds, being electrically neutral, interact with the defects only by the way of the thermodynamic potentials. Their effect is implicitly taken into account if one uses reduced quantities, expressing the difference of a physical parameter between a defect and the normal species. Thus, for an ideal mixture, the following expression for the free enthalpy holds:

\[
g_i = g_i^0(p, T) + kT \log c_i
\]  

(2.6)

with the meaning: free enthalpy of the defect \( i \) minus free enthalpy of a regular water molecule, respectively of a regular bond.
When the chemical equilibrium is established, the $c_i$ are functions of the pressure and the temperature; in the expression
\[
\text{grad } g_i = v_i \text{grad } p - s_i \text{grad } T + k T \frac{\partial}{\partial T} \text{grad } \log c_i
\]
the coefficients are
\[
v_i = v_i^0 + k T \frac{\partial}{\partial p} \log c_i \quad \text{and} \quad s_i = s_i^0 - \frac{\partial}{\partial T} (k T \log c_i).
\]
The enthalpy becomes with equation (2.6)
\[
h_i = g_i + T \cdot s_i = h_i^0 - k T^2 \frac{\partial}{\partial T} \log c_i.
\]
Moreover, the reactions (2.2) and (2.3) require
\[
g_1 + g_2 = 0 \quad \text{and} \quad g_3 + g_4 = 0,
\]
so that the concentrations are given by
\[
c_1 c_2 = \exp\left[\frac{(-g_1^0 - g_2^0)}{k T}\right] \quad \text{and} \quad c_3 c_4 = \exp\left[\frac{(-g_3^0 - g_4^0)}{k T}\right].
\]

3. Entropy production, forces and currents

According to the thermodynamics of irreversible processes, the variation with time of the entropy $S$ per unit volume is given by
\[
\frac{dS}{dt} = -\text{div } J_S + \dot{s}.
\]
$J_S$ is the entropy current:
\[
J_S = (j_q - \sum_i j_i g_i)/T.
\]
$j_q$ being the heat current and $j_i$ the currents of the different species; $\dot{s}$ is the internal entropy production by the irreversible processes, and in the case of chemical equilibrium it has the form
\[
T \dot{s} = \sum_i j_i \cdot x_i + j_q \cdot x_u.
\]
The $x_i$ are generalized forces, conjugated to the currents $j_i$, and amount to
\[
x_i = f_i - T \text{grad } (g_i/T) \quad \text{and} \quad x_u = -\left(\text{grad } T\right)/T,
\]
where $f_i$ is the external force applied to the species $i$.

The currents and the forces are connected by linear relations:
\[
j_i = \sum_k \lambda_{ik} x_k + \lambda_{iu} x_u,
\]
\[
j_q = \sum_k \lambda_{uk} x_k + \lambda_{uu} x_u,
\]
the coefficients $\lambda_{ik}$ obeying to the Onsager reciprocity relations
\[
\lambda_{ik} = \lambda_{ki}, \quad \lambda_{ui} = \lambda_{iu}.
\]

If $k$ forces (e.g. $x_1, x_2, \ldots, x_k$) are held at fixed values, the system tends toward a so called steady state of order $k$. The free forces $(x_{k+1}, x_{k+2}, \ldots, x_n)$ take then values that minimalize the entropy production $\dot{s}$, and the conjugated currents $(j_{k+1}, j_{k+2}, \ldots, j_n)$ vanish.
These relations are of course valid for ice, but a supplementary term has to be taken into account in the entropy production, for the following reason. When the defects move, they displace protons along or between the bonds, and thus change their configuration. If the defect motion is at random (as it is the case when no external force is applied) the lattice disorder remains the same, but if the motion has a net component in a certain direction, then a certain order appears, which in turn implies a modification of the entropy. The influence of the different defects has been analysed previously [7, 11, 15, 18] and can be summarized in the following consideration (Fig. 1). A current of positive ions pushes the protons forward along the bonds, from the "bottom" to the "top" of the bonds, and a current in the same direction of negative ions pushes them backward. Conversely, a current of D-defects displaces the protons sitting at the "top" of the bonds to the "bottom" of a next bond (in the direction of the current) while a current of L-defects does the opposite. It is then convenient to introduce the total number per unit volume \( \nu \) of protons that have been displaced to the "top" of the bonds and the direction of the displacement with the "configuration vector" \( \Omega \):

\[
\Omega = \int_0^t (j_1 - j_2 - j_3 + j_4) \, dt = \int_0^t \sum_{k=1}^4 \eta_k j_k \, dt, \tag{3.8}
\]

which expresses the different influences of the defects.

For the parameters \( \eta_k = \pm 1 \), a physical interpretation will be found later. The displacement of a proton along a bond or between two bonds being accompanied by a jump of a defect over a step of length \( \Delta l \), depending of the direction, the configuration vector \( \Omega \) is then obviously equal to the product of this step length by the number \( \nu \):

\[
|\Omega| = \nu \cdot \Delta l. \tag{3.9}
\]

When the currents are parallel to the c-axis, the shortest period along this axis is between two neighboring hexagon layers, and it can be taken as a unit step (see Fig. 1):

\[
\Delta l_{\parallel} = \frac{4}{3} r_0. \tag{3.10}
\]

For each step, there is one proton moved along a parallel bond and one proton moved on an oblique bond. The number of these bonds per unit volume is \( N_0/2 \) and \( 3N_0/2 \) respectively.
Thus, in the random configuration at the beginning of the process ($t = 0$), $N_0/4$ parallel bonds have their proton in the low site, and $N_0/4$ in the high site. When $v_\parallel$ protons have been displaced ($t > 0$), these numbers change to $(N_0/4) - v_\parallel$ and $(N_0/4) + v_\parallel$, respectively. The number of configurations yielding such numbers is

$$\frac{(N_0/2)!}{[(N_0/4) - v_\parallel]![(N_0/4) - v_\parallel]!},$$

and there is an analogous formula for the oblique bonds. We can assume that each configuration has the same a priori probability: there is practically no short range interaction between the defects as a result of the Bernal-Fowler rules, because of their very low concentrations ($c_t \leq 10^{-6}$). In this case the probability $\mathcal{P}_\parallel$ to get such a number $v_\parallel$ is given by

$$\log \mathcal{P}_\parallel = \text{const} - \log \left[ \left( \frac{N_0}{4} - v_\parallel \right)! \left( \frac{N_0}{4} - v_\parallel \right)! \right]$$

$$- \log \left[ \left( \frac{3N_0}{4} + v_\parallel \right)! \left( \frac{3N_0}{4} + v_\parallel \right)! \right].$$

(3.11)

As the numbers are large, the Stirling formula can be used for the factorials and it is sufficient to consider only the first non vanishing terms of the Taylor developments if we assume that the deviation from the random distribution is small.

The entropy per unit volume $s_\parallel = k \log \mathcal{P}_\parallel$ can be calculated and has then the value

$$s_\parallel = - \frac{16}{\sqrt{3}} k v_\parallel^2/n_0 = - \frac{8}{\sqrt{3}} k r_{00} \Omega_\parallel^2.$$  

(3.12)

When the currents are perpendicular to the c-axis, e.g. in the (2110) direction, the protons are displaced along the sides of the lattice hexagons, and the unit step can be taken as

$$\Delta l_\perp = r_{00} \sqrt{2/3},$$

(3.13)

each step corresponding this time to the displacement of a single proton. As the number of the considered bonds is $N_0$, the probability is given by

$$\log \mathcal{P}_\perp = \text{const} - \log \left[ \left( \frac{N_0}{2} + v_\perp \right)! \left( \frac{N_0}{2} - v_\perp \right)! \right],$$

(3.14)

and the entropy per unit volume by

$$s_\perp = - 2 k v_\perp^2/N_0 = - \frac{8}{\sqrt{3}} k r_{00} \Omega_\perp^2.$$  

(3.15)

A comparison between (3.12) and (3.15) shows the scalar character of the entropy, and its production per unit time and volume can then be written:

$$\dot{s} = - \frac{16}{\sqrt{3}} k r_{00} \Omega \cdot \dot{\Omega}.$$  

(3.16)

After multiplication with the absolute temperature $T$ and defining:

$$\Phi = (16/\sqrt{3}) k T r_{00},$$  

(3.17)

one finally obtains with equation (3.8)

$$T \dot{s} = - \Phi \Omega \cdot \sum_{k=1}^{4} \eta_k \dot{j}_k,$$

(3.18)

an expression that has to be introduced in (3.3).
Assuming that the only external force is the electric field $F$, acting on the charges $e_i$, the forces are then:

$$x_i = e_i F - \eta_i \Phi \Omega - T \, \text{grad} \left( \frac{g_i}{T} \right).$$  \hspace{1cm} (3.19)

We substitute for the $\lambda_{tu}$ the transport heat $q^*_k$ defined by

$$\lambda_{tu} = \sum_k \lambda_{tk} q^*_k.$$  \hspace{1cm} (3.20)

They are the heat transported by the currents $j_k$ when the temperature gradient vanishes:

$$j_q = \sum_k j_k \, q^*_k + x_u (\lambda_{uu} - \sum_{i,k} \lambda_{tk} q^*_i q^*_k).$$  \hspace{1cm} (3.21)

On the other hand, the third term in (3.19) can be written

$$T \, \text{grad} \left( \frac{g_i}{T} \right) = v_i \, \text{grad} \, p - h_i \, \text{grad} \, T + \text{grad} \left( \frac{v_i}{T} \right) \frac{v_i}{T},$$  \hspace{1cm} (3.22)

so that it is possible to perform the following variable transformation ($I = \text{electric current}$):

$$J_i = j_i$$  

$$X_i = - \text{grad} \left( \frac{v_i}{T} \right) \frac{v_i}{T} \quad (i = 1, 2, 3, 4)$$  

$$J_5 = \sum_{i=1}^{4} j_i e_i = I$$  

$$X_5 = F$$  

$$J_6 = \sum_{i=1}^{4} j_i \eta_i = \dot{\Omega}$$  

$$X_6 = - \Phi \Omega$$  \hspace{1cm} (3.23)

$$J_7 = \sum_{i=1}^{4} j_i v_i$$  

$$X_7 = - \text{grad} \, p$$  

$$J_8 = j_q - \sum_{i=1}^{4} j_i h_i$$  

$$X_8 = - \left( \text{grad} \, T \right) / T$$

which leaves the entropy production in the same form

$$T \dot{s} = \sum_{i=1}^{8} J_i \cdot X_i,$$  \hspace{1cm} (3.24)

but lets quantities appear which can be determined experimentally. The new currents and forces obey also the relation

$$J_i = \sum_{k=1}^{8} L_{ik} X_k \quad (i = 1, 2, \ldots, 8)$$  \hspace{1cm} (3.25)

with

$$L_{ik} = L_{ki}.$$  \hspace{1cm} (3.26)

These new coefficients are related to the other ones by linear relations that are easy to calculate.

The electric charges we have introduced here have a dynamical meaning, like it was the case in a previous paper [11]. When a defect state jumps on a neighboring lattice site a distance $r$ apart, the proton jump is accompanied by a displacement of the neighboring nuclei (O and H) and of the molecular electronic clouds. The defect charge is then defined as the volume integral of every charge element times its displacement, the whole divided by the distance $r$. If the spatial character of this relation is considered, we see that the charge $e_i$ transforms a vector (the defect state displacement) into another one (the integral of the product charge times
displacement). If the structure possesses enough symmetry, the two vectors can be parallel, and $e_i$ is a scalar. But, as we shall see later, it need not to be the case, and the dynamical defect charge has rather to be considered as a tensor.

Apart of the obvious symmetry relations between the charges

\[
e_1 = -e_2 = e_\pm = \text{ionic charge},
\]

\[
e_3 = -e_4 = e_{DL} = \text{valence defect charge}
\]

there is a third one for the following reason. When a net protonic charge is transported through the lattice, it has to use the ionic as well as the valence defect mechanism. Two defect charges $e_1$ (or $e_2$) and $e_3$ (or $e_4$) move together through the lattice, in the same direction like the proton, if they are positive ($e_1, e_3$), and in the opposite direction, if they are negative ($e_2, e_4$). Thus their algebraic combination must give the protonic charge, resulting in the equality:

\[
e_\pm + e_{DL} = e = \text{protonic charge}.
\]

Before we proceed to the analysis of the system it is convenient to examine at first the electrical properties alone, as they are relatively easy to measure and give physical interpretations for the coefficients $L_{ik}$.

4. Electrical properties

We shall start from the second form (3.24) of the entropy production and assume that only $X_6 = -\Phi \Omega$ is free, the other forces being held at the values

\[
X_i = 0 \quad (i = 1, 2, 3, 4)
\]

\[
X_5 = F \neq 0
\]

\[
X_7 = X_8 = 0.
\]

(4.1)

If $F$ has a constant value, the system tends toward a steady state of the seventh order, where $J_6 = \dot{\Omega}$ vanishes. The equations (3.25) reduce to

\[
\dot{\Omega} = J_6 = L_{65} F - L_{66} \Phi \Omega = 0,
\]

\[
I = J_5 = L_{55} F - L_{56} \Phi \Omega,
\]

(4.2)

the solution being

\[
\Phi \Omega = (L_{56}/L_{66}) F,
\]

\[
I = (L_{55} - L_{56}^2/L_{66}) F.
\]

(4.3)

(4.4)

Let us define a “polarization charge” $e_p$ where

\[
e_p \equiv L_{56}/L_{66},
\]

(4.5)

for which a physical interpretation will be found later. We then have for the static conductivity $\sigma_0$:

\[
\sigma_0 = L_{55} - L_{56}^2/L_{66} = \sum_{i,k=1}^4 \lambda_{ik} e_k (e_k - e_p \eta_k).
\]

(4.6)

If $t_i$ is the static transport number for the defect $i$, we have also

\[
j_i = \frac{t_i}{e_i} I \quad \text{and} \quad \sum_{i=1}^4 t_i = 1,
\]

(4.7)

and from equation (4.6) we obtain

\[
t_i = \sigma_0^{-1} e_i \sum_{k=1}^4 \lambda_{ik} (e_k - e_p \eta_k).
\]

(4.8)
It is easy to verify that
\[ t_1 + t_2 = e_{\pm}/e \quad \text{and} \quad t_3 + t_4 = e_{\text{DL}}/e, \] (4.9)
as it should be, since in the d.c. process the protons are carried alternatively by
the ions and by the valence defects. The currents conjugated to the pressure and
temperature gradients are proportional to the electric current:
\[ \mathbf{J}_7 = I \sum \frac{t_i}{e_i} \mathbf{v}_i, \quad \mathbf{J}_8 = I \sum \frac{t_i}{e_i} (q_i^* - h_i) \] (4.10)
and
\[ \mathbf{j}_q = \mathbf{J}_8 + \sum j_i h_i = I \cdot \sum \frac{t_i}{e_i} q_i^* \]
and express the volume and heat transport by the defects.

If the field is varying with time, the expressions (4.2) still hold, but \( \dot{\mathbf{Q}} \) does
not vanish. With a periodic time dependence \( \exp(i \omega t) \), the system becomes:
\[ 0 = L_{56} F - (L_{66} \Phi + i \omega) \Omega, \]
\[ I = L_{55} F - L_{56} \Phi \Omega, \] (4.11)
and the a.c. conductivity \( \sigma \) is then given by
\[ \sigma - \sigma_0 = (\sigma_\infty - \sigma_0) (1 + 1/i \omega \tau_p)^{-1} \] (4.12)
with
\[ \sigma_\infty = L_{55} = \sum_{i,k=1}^{4} \lambda_{ik} e_i e_k \] (4.13)
and
\[ 1/\tau_p = \Phi L_{66} = \Phi \sum_{i,k=1}^{4} \lambda_{ik} \eta_i \eta_k. \] (4.14)
This indicates a Debye mechanism with a single relaxation time \( \tau_p \). Transport
numbers \( t' \) for the high frequency conduction can also be defined:
\[ t'_i = \sigma_\infty^{-1} e_i \sum_{k=1}^{4} \lambda_{ik} e_k = \sigma_i/\sigma_\infty \] (4.15)
the \( \sigma_i \) being the quantities previously defined as the specific conductivities [11].

Introducing a global parameter for the interaction between ions and bonds
\[ \lambda' = \lambda_{13} - \lambda_{14} - \lambda_{23} + \lambda_{24} \] (4.16)
and the compound conductivities
\[ \sigma_{\pm} = \sigma_1 + \sigma_2 \quad \text{and} \quad \sigma_{\text{DL}} = \sigma_3 + \sigma_4, \] (4.17)
the static conductivity can then be expressed by:
\[ \frac{\varepsilon^2}{\varepsilon_0} = \frac{\varepsilon^2}{\varepsilon_{\infty}} + \frac{\varepsilon^2_{\text{DL}}}{\sigma_{\text{DL}}} - \lambda' e_{\pm} e_{\text{DL}} (\sigma_{\pm} e_{\text{DL}} - \sigma_{\text{DL}} e_{\pm})^2 (\sigma_{\pm}^2 + \sigma_{\text{DL}}^2 - \lambda' \sigma_{\infty} \sigma_{\pm} \sigma_{\text{DL}} e_{\pm} e_{\text{DL}})^{-1} \] (4.18)
which is about the same formula obtained previously (with exception of \( \lambda' \)) and
shows that the d.c. conductivity is determined by the smallest of the compound
specific conductivities.

The dielectric properties can easily be deduced. Denoting with \( \varepsilon \) the con-
tribution of the defects to the dielectric constant (the high frequency constant
\( \varepsilon_\infty = 3.18 \) has to be added to obtain the measured constant of the material),
equation (4.12) yields:
\[ \varepsilon_0 \varepsilon = (\sigma - \sigma_0)/i \omega = \varepsilon_0 \varepsilon_0/(1 + i \omega \tau_p) \] (4.19)
with \( \varepsilon_0 \varepsilon_s = (\sigma_{\infty} - \sigma_0) \tau_p = e_p^2 / \Phi . \) (4.20)

To have a physical interpretation for the charge \( e_p \), we consider the static polarisation \( P_s \) given by

\[ P_s = \varepsilon_0 \varepsilon_s F = (e_p^2 / \Phi) F \]  

but according to (4.3) and (4.5)

\[ P_s = e_p \Omega . \]  

(4.22)

On the other hand, the contribution of \( \Omega \) to the force acting on a defect is according to equations (3.19) and (4.22)

\[ (x_k)_\Omega = - \eta_k \Phi \Omega = ( - \eta_k e_p ) ( e_p \Omega ) / \varepsilon_0 \varepsilon_s . \]  

(4.23)

Thus \( e_p \) is the factor relating the reversible electric polarisation of the lattice with the order of the proton configuration. It can be interpreted as a “quantum of polarisation”, as it was first pointed out by Onsager [15] for the case of pure ice. The entities \( - \eta_k e_p \) are “polarisation charges” attached to the defects, on which the polarisation \( P \) exerts a force \( - \eta_k e_p P / \varepsilon_0 \varepsilon_s \), and they are also the sources of the polarisation whenever the chemical equilibrium is established: we have

\[ \dot{n}_k + \text{div} j_k = 0 \]  

(4.24)

and consequently

\[ \text{div} P = e_p \text{div} \Omega = e_p \sum_k \eta_k \int_0^t \text{div} j_k \, dt = \sum_k n_k ( - \eta_k e_p ) . \]  

(4.25)

The polarisation charge \( e_p \) can be expressed by the specific conductivities:

\[ e_p = (\sigma_{\pm} - \sigma_{DL}) \left( \frac{\sigma_{\pm}}{\varepsilon_0} + \frac{\sigma_{DL}}{\varepsilon_{DL}} - \frac{\lambda' e^2}{\varepsilon_0 \varepsilon_{DL}} \right)^{-1} . \]  

(4.26)

It is obviously not a constant determined only by the lattice but it depends of the relative amount and mobilities of the ions relative to the valence defects. If the specific conductivities are matched so that

\[ \sigma_{\pm} / \varepsilon_0 = \sigma_{DL} / e_{DL} , \]  

(4.27)

the polarisation charge disappears, and with it the static dielectric constant \( \varepsilon_s \) and the difference between the high frequency and the d.c. conductivities. In certain cases, the proton motion is not caused by an external force as \( F \), but rather by internal gradients; the order of the proton configuration, defined by \( \Omega \), may then still have a finite value, but it produces no electrical polarisation. The sign and the absolute value of \( e_p \) are different if the ions or if the valence defects are “majority carriers”. In the first case, one has:

\[ \sigma_{\pm} \gg \sigma_{DL}, \quad e_p = e_\pm \left( 1 - \frac{e_\pm}{e_{DL}} \cdot \frac{\lambda' e^2}{\sigma_{\pm}} \right)^{-1} \cong e_\pm , \]  

(4.28)

and in the second case

\[ \sigma_{DL} \gg \sigma_{\pm}, \quad e_p = - e_{DL} \left( 1 - \frac{e_{DL}}{e_\pm} \cdot \frac{\lambda' e^2}{\sigma_{DL}} \right)^{-1} \cong - e_{DL} . \]  

(4.29)

The approximations are good, because \( \lambda' \) is of the order of the smallest of \( \sigma_{\pm} \) and \( \sigma_{DL} \).

Up to this point, we have made no statement on the tensorial character in space of the quantities \( \lambda_{ik}, L_{ik}, \Phi, \sigma_i \), etc. As long as there is no experimental
reason to assume that they are tensors, they may be of course considered as scalars. According to the present state of empirical knowledge, no measurable electric anisotropy has been found in ice, except in the optical range and for the static dielectric constant [10], where measurements at \(-10.9^\circ\text{C}\) give (with \(\varepsilon_\infty = 3.18\)):

\[
\varepsilon_{a\perp} = 93 \quad \text{and} \quad \varepsilon_{a\parallel} = 109.5
\]

perpendicular and parallel to the \(c\)-axis. The anisotropy amounts to

\[
\frac{\varepsilon_{a\parallel} - \varepsilon_{a\perp}}{(\varepsilon_{a\parallel} + \varepsilon_{a\perp})/2} = 16\%.
\]

Looking at equation (4.20), we have to determine what quantity on the right side could be a tensor. The coefficient \(\Phi\) defined by equation (3.17) contains, apart of numbers and the thermal energy \(kT\), the distance \(r_{00}\) between two oxygen atoms. The lattice has been assumed to be ideal, that is built up of quite regular tetrahedra, with the same value of \(r_{00}\) for all the bonds, so that \(\Phi\) should be a scalar. However, the real ratio between the two lattice constants \(c/a\) has at \(0^\circ\text{C}\) the value of 1.629, which differs from the ideal ratio 1.633 [7]. The neutron diffraction experiments in heavy ice [16] indicate that the bonds parallel to the \(c\)-axis are somewhat shorter than the oblique ones. If all the discrepancy for the \(c/a\) ratio is caused by a similar reason in ordinary ice, we obtain an anisotropy of 0.2\% with the right sign. But this is roughly eighty times too small to explain by itself the anisotropy of \(\varepsilon_a\). Therefore, we shall neglect this small deviation and take \(\Phi\) as a scalar.

The only possibility that remains is that \(\varepsilon_p\) is a tensor with an anisotropy of 8\%. As the results above concern pure ice, we know that the valence defects are the majority carriers [11] by a consideration not invalidated by the present theory. Thus we have to apply the relation shown in equation (4.29). The coefficient \(\lambda'\) contains terms that appear in the ionic as well as in the valence defect conductivity, but as \(\sigma_\pm \ll \sigma_{DL}\) this requires that \(e^2 \lambda' \ll \sigma_{DL}\). The correction factor in \(\lambda'\) is thus much smaller than unity, and it cannot be made responsible for the anisotropy. We have therefore to consider both \(\sigma_{DL}\) and \(\varepsilon_{\pm}\) as tensors, because the relation \(\varepsilon_\pm + \varepsilon_{DL} = \varepsilon\) has to be valid in every direction.

We shall assume that the \(\lambda_{ik}\) are spatial scalars, but even in this case the specific conductivities are tensors, as they contain products \(e_i e_k\). Their anisotropy has not yet been observed, being at the limit of the experimental accuracy. If it should become possible, it would give some information about the interaction parameter \(\lambda'\). From the following expressions

\[
\sigma_\pm = e^{\pm}_\pm (\lambda_{11} - 2\lambda_{12} + \lambda_{22}) + \varepsilon_\pm e_{DL} \lambda', \quad \sigma_{DL} = e_{DL}^2 (\lambda_{33} - 2\lambda_{34} + \lambda_{44}) + \varepsilon_{\pm} e_{DL} \lambda',
\]

we see that, if \(\lambda'\) vanishes, the anisotropy of the partial conductivities is twice the one of the corresponding defect charge, but if \(\lambda'\) is large enough, this does not hold. It can be shown that the anisotropy of all the electric parameters connecting vectors together, as the dielectric constant, the d.c. and high frequency conductivities must have twice the anisotropy of the majority charge provided \(\lambda'\) is small.
The experimental values (4.30) allow the defect charges to be calculated:

\[ \varepsilon_{\text{DL}} = 0.55 \varepsilon, \quad \varepsilon_{\text{DL} \perp} = 0.51 \varepsilon, \]

\[ \varepsilon_{\parallel} = 0.45 \varepsilon, \quad \varepsilon_{\perp} = 0.49 \varepsilon. \]  

These values are somewhat different of the ones estimated earlier [11, 15]. The quantities used in the formula, as \( r_0, kT, \varepsilon_0 \) and \( \varepsilon_\parallel \) are given by the experiments, and the factor \( 16J/3 \) occurring in \( \Phi \) is determined by a statistical consideration; the influence of the factor \( \lambda' \) in equation (4.29) can also be neglected for the reason given above, so that it seems that the present values are reliable.

From the consideration of the end of Section 3, we know that the cause of the anisotropy has to be looked for in the electronic and ionic motions in the neighborhood of the moving defect. In this respect, it has to be noticed that there are two different types of bonds: Those parallel to the c-axis (p) which connect two molecules in a mirror-symmetrical position and those oblique to the c-axis (o), which connect two molecules in a central-symmetrical position. Therefore, if the current is along the c-axis, the defects use alternatively p and o bonds, but if it is normal to the c-axis, they use only o bonds. This fact could be the reason of the anisotropy, but we mention it here just as a hypothesis which has of course to be verified by a calculation with a suitable microscopical model.

5. Field and charge relaxation

In the preceding section, the field was an independent variable, and a single relaxation time \( \tau_p \) appeared. When the field is dependent of other quantities, the relaxation mechanism is different because of the coupling between current and field. If \( \varrho \) is the specific electric charge, the continuity and the Poisson equations

\[ \dot{\varrho} + \text{div} \mathbf{I} = 0 \quad \text{and} \quad \varrho - \varepsilon_0 \varepsilon_\infty \text{div} \mathbf{F} = 0 \]  

give after elimination of \( \varrho \) the relation:

\[ -\varepsilon_0 \varepsilon_\infty \dot{\mathbf{F}} = \mathbf{I} - \mathbf{I}' \quad \text{and} \quad \text{div} \mathbf{I}' = 0, \]

where \( \mathbf{I}' \) is an arbitrary current injected in the crystal from the outside, and can be disregarded in the present case. The system (4.2) takes the homogenous form:

\[ \varepsilon_0 \varepsilon_\infty \mathbf{\ddot{F}} + L_{55} \mathbf{F} - L_{56} \Phi \mathbf{\Omega} = 0 \]

\[ -\Phi \mathbf{\Omega} + L_{56} \mathbf{F} - L_{66} \Phi \mathbf{\Omega} = 0. \]

Introducing the following frequencies:

\[ \omega_\infty = \sigma_\infty / \varepsilon_0 \varepsilon_\infty \quad \text{and} \quad \omega_0 = \sigma_0 / \varepsilon_0 \varepsilon_\infty \]  

the relaxation times \( \tau \) are given by the equation

\[ 1/\tau^2 - (1/\tau) (1/\tau_p + \omega_\infty) + \omega_0 / \tau_p = 0. \]  

As

\[ \tau_p \omega_\infty \gg 1 \quad \text{and} \quad 4 \omega_0 / \tau_p \omega_\infty^2 \ll 1, \]  

it is possible to write the two solutions as

\[ 1/\tau_f \approx \omega_\infty + (1/\tau_p) (1 - \omega_0 / \omega_\infty) \quad \text{and} \quad 1/\tau_g \approx \omega_0 / \tau_p \omega_\infty. \]

The first of the relaxation times is always nearly equal to \( 1/\omega_\infty \). As \( \sigma_\infty \) is generally large and \( \varepsilon_\infty \) is small, \( \tau_f \) has a small value, of the order of \( 10^{-5} \) to \( 10^{-6} \) sec. The
second relaxation time is larger. It varies between the polarisation relaxation time $\tau_p$ of the order of $10^{-4}$ to $10^{-5}$ sec if there is no majority character, to a much larger value of $\varepsilon_0 \varepsilon_s / \sigma_0$ when $\sigma_0 \ll \sigma_\infty$. For pure ice at $-10^\circ$C for example, we have

$$\tau_p = 5 \cdot 10^{-5} \text{ sec},$$

$$\sigma_\infty = 2 \cdot 10^{-5} \; \Omega^{-1} \; \text{m}^{-1} \quad \text{and} \quad (5.8)$$

$$\sigma_0 = 1 \cdot 10^{-7} \; \Omega^{-1} \; \text{m}^{-1}$$

so that

$$\tau_s \approx 10^{-2} \text{ sec}.$$

If stepwise varying forces are applied to the crystal, the electric field and the polarisation will reach their new equilibrium value partly with a fast ($\tau_f$) and partly with a slow process ($\tau_s$). The amplitude ratio for these processes depends of course of the initial conditions, but the amplitude of the slow decay will be generally smaller.

Charge relaxation is the process which governs the disappearance of a net electric charge localized somewhere in the lattice, and distributed on the different defects. The distribution depends upon the method used to put the charge into the lattice. For example, a cluster of protons projected suddenly onto a specimen might subsist there partially in the form of equal overconcentrations of positive ions and D-defects, if the protons are trapped by the electron clouds in the regular hydrogen sites. The knowledge of the charge relaxation is of prime interest for the design of drift measurements to obtain directly the mobilities. Such measurements are possible only if the charge packets remain detectable during a certain time, so that the d.c. drift field needs not to be too large. It is known [5] that the chemical recombination time is much too short for a drift measurement, so that a simple perturbation of the chemical equilibrium would not work. However, if a net charge is present, the local chemical recombination alone cannot make it disappear: it must be smeared out by diffusion and by the self produced electric field. Once the chemical equilibrium is established, if the charge is not too concentrated, the diffusion effect can be neglected as long as the overall cluster dimension is at least of the order of the Debye length $l_D$

$$l_D \approx (\varepsilon_0 \varepsilon_\infty k T / e^2 n_k)^{1/2}.$$

But the charges are the sources of the electric field, so that both will disappear together, that is, with the two relaxation times $\tau_f$ and $\tau_s$ (5.7). A simple calculation gives the result ($\varrho_0 =$ initial charge density)

$$\varrho / \varrho_0 = (\alpha_f \cdot e^{-t / \tau_f} + \alpha_s \cdot e^{-t / \tau_s}) (\alpha_f + \alpha_s)^{-1}$$

with

$$\alpha_f = \omega_\infty (1 - \omega_0 / \omega_\infty^0) \quad \text{and} \quad \alpha_s = (1 / \tau_p) (1 - \omega_0 / \omega_\infty).$$

If the majority character is pronounced ($\sigma_\infty \gg \sigma_0$), equation (5.10) reduces to

$$\varrho / \varrho_0 = \left(1 - \varepsilon_\infty / \varepsilon_s \right) e^{-t / \tau_s} + \varepsilon_\infty / \varepsilon_s e^{-t / \tau_s}.$$  

Thus, for pure ice, only a fraction of about 1/28 of the charge is detectable during the longer time $\tau_s$. This does not a priori exclude a drift experiment, but requires a sensitive charge detector and an efficient proton source.
6. Electrostatic interaction energy

Until now it has been assumed that the charges are so far away one from another that they do not interact electrostatically. This does not however correspond to reality, because a charge has always a certain cloud of opposite polarity around it which screens its electrostatic potential. This problem has been solved for pure ice by Onsager and Dupuis [15] who have extended the Debye-Hückel theory to the case where not only the electrostatic potential $\psi$ has to be considered, but also the polarisation potential $\chi$. This can be generalized here by introducing the variable polarisation charges $-\eta_k e_p$, so that the total energy of a defect is

$$W_k = e_k \psi + \eta_k e_p \chi$$  \hspace{1cm} (6.1)

if

$$\text{grad} \, \chi = P_3/\varepsilon_0 \varepsilon_s.$$  \hspace{1cm} (6.2)

From the Poisson equation:

$$\Delta \psi = -(1/\varepsilon_0 \varepsilon_\infty) \sum n_k n_k$$

and

$$\Delta \chi = -(1/\varepsilon_0 \varepsilon_s) \sum n_k \eta_k e_p$$  \hspace{1cm} (6.3)

with

$$n_k(W_k) = n_k \exp(-W_k/kT) \approx n_k(1 - W_k/kT)$$  \hspace{1cm} (6.4)

we obtain a system of differential equations analogous to those found by Onsager and Dupuis:

$$\varepsilon_0 \varepsilon_\infty kT \Delta \psi = \psi \sum n_k e_k^2 + \chi \sum n_k \eta_k e_p,$$

$$\varepsilon_0 \varepsilon_s kT \Delta \chi = \psi \sum n_k e_k \eta_k e_p + \chi \sum n_k \eta_k e_p^2.$$  \hspace{1cm} (6.5)

with the limit conditions (spherical symmetry):

$$\lim_{r \to 0} \psi(r) = e_k/4 \pi \varepsilon_0 \varepsilon_\infty r \quad \lim_{r \to \infty} \psi(r) = 0,$$

$$\lim_{r \to 0} \chi(r) = \eta_k e_p/4 \pi \varepsilon_0 \varepsilon_s r \quad \lim_{r \to \infty} \chi(r) = 0.$$  \hspace{1cm} (6.6)

The general solution is of the form $e^{-\kappa r}/r$, where $\kappa$ is an inverse Debye length. Let us introduce $\varepsilon_{sp} \approx \varepsilon_{DL}^0 (\varepsilon_0 \Phi)^{-1}$ as the dielectric constant of the pure ice, and remember that the concentration is always higher for the valence defects than for the ions, even if the latter are majority carriers, because of their much larger mobility. The solution for $\kappa$ is then

$$\kappa_1^0 = \kappa^2 \approx (n_3 + n_4) \varepsilon_{DL}^0 \left( \frac{1}{\varepsilon_{sp}} + \frac{1}{\varepsilon_\infty} \right) (\varepsilon_0 k T)^{-1} = \frac{16}{9} (n_3 + n_4) r_{00} (1 + \varepsilon_{sp}/\varepsilon_\infty)$$  \hspace{1cm} (6.7)

and $\kappa_2^0 \approx 0$.

To avoid a divergence in $\chi$ when the polarisation charge vanishes, we consider instead the product $e_p \chi$ and obtain

$$\psi_k r = \frac{(e_k + \eta_k e_{DL})(1 - e^{-\kappa r})}{4 \pi \varepsilon_0 (\varepsilon_{sp} + \varepsilon_\infty)} + \frac{e_k e^{-\kappa r}}{4 \pi \varepsilon_0 \varepsilon_\infty}$$  \hspace{1cm} (6.8)

and

$$e_p \chi_k r = \frac{e_{DL}(e_k + \eta_k e_{DL})(1 - e^{-\kappa r})}{4 \pi \varepsilon_0 (\varepsilon_{sp} + \varepsilon_\infty)} + \frac{e_{DL}^2 \eta_k e^{-\kappa r}}{4 \pi \varepsilon_0 \varepsilon_{sp}}.$$  \hspace{1cm} (6.9)

In the case of pure ice ($e_p = -e_{DL}$) these expressions reduce to those given by Onsager and Dupuis (with the proper notation change), but in the general case they obviously do not contain any term depending upon the majority character. This results from the assumption that the valence defects are always more numerous than the ions, and the determining quantity in this problem is the concentration and not the conductivity. The potentials $\psi'$ and $\chi'$ produced by the charge
clouds alone are equal to equations (6.8) and (6.9) diminished by the potentials produced by the charge itself, given in equation (6.6). The interaction energy between the charge and its cloud is then

\[ W_k' = e_k \varphi_k'(r = 0) + \eta_k e_p \chi_k'(r = 0) \]  

(6.10)

and amounts to

\[ W_k' = -\frac{\kappa}{4 \pi \varepsilon_0} \left( \frac{e_k \varepsilon_{sp} - e_{DL} \eta_k \varepsilon_\infty}{\varepsilon_\infty (e_{sp} + \varepsilon_\infty)} \right)^2 \approx -\frac{\kappa e_k^2}{4 \pi \varepsilon_0 \varepsilon_\infty} . \]  

(6.11)

The parameter \( \kappa \) can be estimated to \( 3 \cdot 10^7 \text{m}^{-1} \) at \(-10^\circ \text{C} \) in pure ice, so that the interaction energy \( W_k' \) is about \( 3 \cdot 10^{-3} \text{eV} \). The valence defect concentration can be enhanced by a factor of one hundred (with a high concentration of hydrofluoric acid) so that the interaction energy is at most equal to \( kT \). Therefore it is always smaller than the observed enthalpies (which are of the order of 0.3 eV) and, except in the high HF concentration range, it should not influence the dissociation markedly.

7. Steady state processes involving forces other than the electric field

In section 4, only the configuration vector \( \Omega \) was free and among the fixed forces, the electric field alone was not zero. We can now proceed to cases where both \( F \) and \( \Omega \) are free and where one of the other gradients is held at a finite value or where one of the gradients and \( \Omega \) are free and the field is fixed (to obtain the inverse effect). The steady state is then of the sixth order, and two currents have to vanish.

Let us begin with the following case:

\[ \begin{align*}
\operatorname{grad} g_k &= 0, \quad F, \Omega \text{ free} \\
\operatorname{grad} p &= 0, \\
\operatorname{grad} T &= 0.
\end{align*} \]  

(7.1)

We have then the system:

\[ \begin{align*}
I &= -\sum_{k=1}^{4} L_{5k} \operatorname{grad} g_k + L_{55} F - L_{56} \Phi \Omega = 0, \\
\Omega &= -\sum_{k=1}^{4} L_{6k} \operatorname{grad} g_k + L_{65} F - L_{66} \Phi \Omega = 0,
\end{align*} \]  

(7.2)

from which the field can be obtained with equations (2.10) and (4.8):

\[ F = \sum_{k=1}^{4} \left( \frac{t_k}{e_k} \right) \operatorname{grad} g_k = \frac{1}{e} \operatorname{grad} (g_1 + g_3). \]  

(7.3)

As the gradient of the free enthalpy with constant pressure and temperature is produced by a gradient in the chemical composition, we obtain for the electrochemical potential \( U_c \)

\[ U_c = -\sum \left( \frac{t_k}{e_k} \right) g_k = -\frac{1}{e} (g_1 + g_3) \]  

(7.4)

and with equation (2.6)

\[ U_c = -\sum \frac{t_k}{e_k} [g_k^0(p, T) + kT \log c_k] = -\frac{1}{e} [g_1^0 + g_3^0 + kT \log (c_1 c_3)]. \]  

(7.5)
The currents \( j_k \) conjugated to the forces \( \text{grad} \ g_k \) vanish in the steady state; this can be verified by a short calculation. It is useful to transform the expression (7.4) to let the enthalpies \( h_k \) appear rather than the free enthalpies \( g_k \). We have generally
\[
h = g + T s = g - T \frac{\partial g}{\partial T},
\]
so we take the function
\[
U'_c = -T^2 \frac{\partial}{\partial T} (U_c/T) = U_c - T \frac{\partial U_c}{\partial T}.
\]
Because of equation (4.9)
\[
\sum g_k \frac{\partial}{\partial T} \left( \frac{t_k}{e_k} \right) = g_1 \frac{\partial}{\partial T} \left( \frac{t_1}{e_{\text{\pm}}} + \frac{t_2}{e_{\text{\pm}}} \right) + g_3 \frac{\partial}{\partial T} \left( \frac{t_3}{e_{\text{DL}}} + \frac{t_4}{e_{\text{DL}}} \right) = 0
\]
and we obtain finally
\[
U'_c = -\sum \left( \frac{t_k}{e_k} \right) h_k = -\frac{1}{e} (h_1 + h_3),
\]
the enthalpies \( h_k \) being given by equation (2.9) and depending on the chemical constitution. The measurement of \( U'_c \) between two pieces of ice with different doping can give some information on the enthalpies, with certain supplementary hypotheses.

The inverse effect, the isobaric and isothermal production of a concentration gradient by the electric field, is characterized by the following case:
\[
F = 0, \quad \Omega, \quad \text{grad} \ g_k \text{ free}_{(p,T)}
\]
\[
\text{grad} \ p = 0,
\]
\[
\text{grad} \ T = 0
\]
where
\[
j_k = 0 \quad (k = 1, 2, 3, 4), \quad \Theta = 0.
\]
But these equations require that \( I = 0 \), so that the system (7.2) can be used and gives
\[
\text{grad} (g_1 + g_3) = eF.
\]
or with equation (2.6)
\[
\text{grad} \log c_1 + \text{grad} \log c_3 = e F / k T.
\]
With the conditions of chemical equilibrium and of electrical neutrality:
\[
\text{grad} \log (c_1c_2) = \text{grad} \log (c_3c_4) = 0 \quad \text{and}
\]
\[
c_{\text{\pm}}(c_1 - c_2) + e_{\text{DL}}(c_3 - c_4) = 0
\]
the solutions become
\[
\text{grad} \log c_1 = -\text{grad} \log c_2 = \frac{eF}{k T} (c_3 + c_4) e_{\text{DL}}[(c_3 + c_4) e_{\text{DL}} - (c_1 + c_2)e_{\text{\pm}}]^{-1}
\]
and
\[
\text{grad} \log c_3 = -\text{grad} \log c_4 = \frac{eF}{k T} (c_1 + c_2) e_{\text{\pm}}[(c_1 + c_2) e_{\text{\pm}} - (c_3 + c_4) e_{\text{DL}}]^{-1}.
\]
This holds, together with the thermodynamic theory introduced in section 3, only for small deviations from the thermostatic equilibrium, that is for potential differences smaller than \( kT \) (\( \approx 20 \text{ mV} \)). We have seen that the electric current
and also the apparent conductivity must vanish in the steady state. This effect should be difficult to observe because of the space charge developed at the electrodes which are always blocking at such low voltages.

Let us next examine the *mechano-electric effect*:

\[
\begin{align*}
\text{grad } p &= 0, \quad F, \Omega \text{ free} \\
\text{grad } g_k &= 0, \\
(\rho, T) &
\end{align*}
\]

\[
\text{grad } T = 0
\]  \hspace{1cm} (7.17)

with the system

\[
\begin{align*}
I &= L_{55} F - L_{56} \Phi \Omega - L_{57} \text{grad } p = 0, \\
\dot{\Omega} &= L_{65} F - L_{66} \Phi \Omega - L_{67} \text{grad } p = 0,
\end{align*}
\]

\[ \text{the } v_k \text{ being given by equation (2.8). The field is then} \]

\[
F = \text{grad } p \sum_{k=1}^{4} \left( t_k \right) e_k \nu_k,
\]

\[ \text{and the mechano-electric potential} \]

\[
\frac{\partial U_p}{\partial p} = - \sum_{k=1}^{4} \left( t_k \right) e_k \nu_k.
\]

\[ \text{If the electric field is held at zero, the electric current is} \]

\[
I = -\text{grad } p \cdot \sigma_0 \sum\left( \frac{t_k}{e_k} \right) v_k.
\]

We see that the current in the short circuited crystal is the same as if it would be produced by the field of the open circuited crystal.

In the inverse effect, the *electro-osmotic pressure gradient* is free, whereas the field is fixed, and we have

\[
\begin{align*}
J_7 &= L_{75} F - L_{76} \Phi \Omega - L_{77} \text{grad } p = 0, \\
\dot{\Omega} &= L_{65} F - L_{66} \Phi \Omega - L_{67} \text{grad } p = 0,
\end{align*}
\]

yielding

\[
\text{grad } p = \sigma_0 F \left[ \sum \left( \frac{t_k}{e_k} \right) v_k \right] \left( L_{77} - L_{76}^2 / L_{66} \right)^{-1}.
\]

The direct effect \((\partial U / \partial p)_T\) is small; with an estimation of \(v_k \simeq 1/2 N_0 \) and \(t_k \simeq 1/4\), a pressure difference of 100 atmospheres produces only a potential difference of one millivolt due to the small ratio of \(v/e \sim 10^{-10} \text{ m}^3 \text{ A}^{-1} \text{ s}^{-1}\). The coefficient for the inverse effect \((\partial P / \partial U)_T\), can be estimated to be roughly \((\sigma_0 / \sigma_\infty) (e/4 v_k)\), i.e. of the order of 100 atm./Volt.

When the field is fixed, the current \(I\) is related to it with a conductivity \(\sigma_{0p}\) which is smaller than the isobaric conductivity:

\[
(\sigma_0 - \sigma_{0p}) / \sigma_0 = \sigma_0 \left\{ \sum \left( \frac{t_k}{e_k} \right) v_k \right\} \left( L_{77} - L_{76}^2 / L_{66} \right)^{-1} = \left( \frac{\partial P}{\partial U} \right)_T \left( \frac{\partial U}{\partial p} \right)_T.
\]

(7.24)

Although there should not be essential difficulties to measure the direct effect, it is not the case with the indirect effect: the pressure built up by the volume transport is partly compensated by the finite compressibility of the material \(\kappa\), so that a long time is necessary to reach the steady state, in the order of

\[
\kappa e^2 \sigma_\infty (l/v_k)^2
\]

(7.25)
where $l$ is the linear dimension of the crystal. A rough estimate gives something like $10^9$ sec, showing the practical impossibility of the measurement. Moreover, the viscosity of the material might be sufficient in such a long period of time to eliminate completely the pressure difference. The electroosmotic effect defined by $(J_l/I)_{\text{grad }p=0}$ can also be derived from the expression (7.18) and (7.22), but this effect is so small that it does not present any interest.

In the homogenous thermoelectric effect, we have:

$$\text{grad } T \neq 0, \quad F, \Omega \text{ free}$$

$$\text{grad } \varphi_k = 0, \quad (\varphi, T)$$

$$\text{grad } p = 0$$

with

$$I = L_{55} F - L_{56} \Phi \Omega - L_{58} (\text{grad } T)/T = 0,$$

and

$$\dot{\Omega} = L_{65} F - L_{66} \Phi \Omega - L_{68} (\text{grad } T)/T = 0.$$  \hspace{1cm} (7.27)

The field is then

$$F = \frac{\text{grad } T}{T} \sum_{k=1}^{4} \left( \frac{t_k}{e_k} \right) \left( q_k^* - h_k \right),$$

and the homogenous thermoelectric power

$$\left( \frac{\partial U_l}{\partial T} \right) = -\frac{1}{T} \sum_{k} \left( \frac{t_k}{e_k} \right) \left( q_k^* - h_k \right),$$

where $h_k$ is given by equation (2.9). If the crystal is short circuited, the electric current is

$$I = -\sigma_0 \sum_{k} \frac{t_k}{e_k} \left( q_k^* - h_k \right) (\text{grad } T)/T$$

which is the same as if produced by the field in the open circuited crystal.

In the inverse effect, the field is fixed and the temperature gradient free to adjust. According to the equations

$$J_8 = L_{85} F - L_{86} \Phi \Omega - L_{88} (\text{grad } T)/T,$$

and

$$\dot{\Omega} = L_{65} F - L_{66} \Phi \Omega - L_{68} (\text{grad } T)/T$$

it takes then the value

$$\text{grad } T = F \cdot T \sigma_0 \sum \left( \frac{t_k}{e_k} \right) \left( q_k^* - h_k \right) (L_{88} - L_{88}/L_{86})^{-1}.$$  \hspace{1cm} (7.32)

The conductivity $\sigma_0 T$ is smaller than the isothermal conductivity $\sigma_0$:

$$(\sigma_0 - \sigma_0 T)/\sigma_0 = \sigma_0 \left[ \sum \left( \frac{t_k}{e_k} \right) \left( q_k^* - h_k \right) \right]^2 (L_{88} - L_{88}/L_{86})^{-1} = \left( \frac{\partial U}{\partial T} \right)_I \left( \frac{\partial T}{\partial U} \right)_J.$$  \hspace{1cm} (7.33)

This has the same form as in equation (7.24).

The quantities $q_k^* - h_k$ can be interpreted in the following way. We have seen in equation (3.21) that the $q_k^*$ are the heats transported by the currents $j_k$ with vanishing temperature gradient. Thus, they consist in the enthalpy $h_k^0$ which the defect always carries with itself, and in the mobility activation energy $w_k^*$ which is necessary for the defects to jump from one lattice site to the other:

$$q_k^* = w_k^* + h_k^0.$$  \hspace{1cm} (7.34)
We have according to (2.9)
\[ q_k^* - h_k = u_k^* + h_k^0 - h_k = u_k^* + k T^2 \frac{\partial}{\partial T} \log c_k. \tag{7.35} \]

As the last term is the enthalpy governing the temperature dependence of the concentration, the whole expression is the activation energy for the specific conductivity:
\[ q_k^* - h_k = -k T \log \sigma_k \tag{7.36} \]
and it can be determined experimentally under certain circumstances. As it is of the order of 0.5 eV, the thermoelectric effect amounts to about 2 mV/°C, but the inverse effect is quite smaller (about 10⁻⁸°C/V) because the denominator in (7.32) contains the thermal conductivity of the lattice, many orders of magnitude larger than the heat transport by the defects.

In the isothermal case, the heat current is given by
\[ j_q = j_S + \sum j_k h_k = I \sum \left( \frac{t_k}{e_k} \right) q_k^*. \tag{7.37} \]
The entropy current being now
\[ T j_S = I \sum \left( \frac{t_k}{e_k} \right) (q_k^* - g_k) \tag{7.38} \]
is constant in the homogenous material; at the junction between two different crystals, the electric current is the same on both sides but its coefficient is not. The divergence of the entropy current produces the Peltier heat defined by the coefficient of proportionality \( \Pi \) with the electric current:
\[ -\Pi = \sum \left( \frac{t_k}{e_k} \right) (q_k^* - g_k). \tag{7.39} \]

With (7.4) and (7.29) it can be written:
\[ -\Pi = T \frac{\partial}{\partial T} (U_c - U_t), \tag{7.40} \]
and finally the Thomson relations give the coefficients for the Seebeck and Thomson effects:
\[ \epsilon = -\Pi/T = \frac{\partial}{\partial T} (U_c - U_t) \]
and
\[ \sigma = -T \frac{\partial}{\partial T} (\Pi/T) = T \frac{\partial^2}{\partial T^2} (U_c - U_t). \tag{7.41} \]

There are other possible effects where any number of forces are free to adjust or are held at finite or zero values. However, they are very small and do not have much experimental interest. Moreover, certain of them might be dominated by the effects which were disregarded in this work, resulting from the elasticity, plasticity and thermal expansion of the lattice.

8. Conclusion

This thermodynamic approach seems to be quite successful to describe the processes occuring in ice. Its advantage against the microscopic theories is the simultaneous coverage of all interesting variables. Once the entropy production is properly expressed, all the possible effects are deduced only by specification of
certain parameters. The thermodynamics is essentially phenomenological, but we have still introduced here a microscopical element in the configuration entropy. However, the defect currents and the factors $\eta_k\Phi$ can be considered as phenomenological parameters; the microscopic consideration is necessary only to determine the value of $\Phi$, and it has therefore no influence on the general properties of the defect system. The peculiar values of the $\eta_k$ describe only the way on which the proton balance is affected, independently of the defect structure. The important thing is not what the defects are but what they do. An interesting point is that the well known electrical properties are correctly described even if the non-diagonal terms $\lambda_{ik}$ are not zero. A superficial estimation could suggest that the interaction between the defects should prevent such simple mechanisms like the Debye relaxation.

The results have to be applied with care, for the following reasons: first, the defect system is described at a determined point on the temperature scale, and only the derivative at this point is taken into account; an extrapolation on a finite temperature range is not allowed a priori. Second, the parameters $\lambda_{ik}$ are functions of the defect concentrations too, and the relations obtained are strictly valid only in a very narrow concentration interval. This does not, of course, prevent to establish functions in large domains, but this has to be done by integration point by point.

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