*F*-center theory, which predicts luminescence near 10 000A with 100 percent efficiency, is not correct. It is possible that a more detailed theoretical investigation of the configuration coordinate curves for the *F* center, both in its ground state and in its excited state, might lead to a better understanding of these results.

## ACKNOWLEDGMENTS

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# Theory of Thermodielectric Effect

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A theory is put forth to explain the electrical effects which accompany phase changes occurring in dielectrics and aqueous solutions. Ionic movement in the interface is treated as a transition between energy levels separated by potential barriers. The height of the barriers and the value of the energy levels are supposed to be different for positive and negative ions. Such a model results in a net current flow across the solid-liquid interface. When the interface moves during a phase change of the system, the excess electric charges thus produced constitute space charges in the solid and surface charges in the liquid. The field of the global charge distribution causes the appearance of the currents and potential differences which have been observed between the plates of a condenser containing the dielectric.

## INTRODUCTION

COSTA RIBEIRO, a Brazilian physicist, while studying electret behavior and related effects, discovered in 1944 that solidification and melting of many dielectrics are accompanied by charge separation.[1] He found that the phenomenon is observed only if the phase change proceeds in an orderly fashion, that is, if a definite phase boundary (or interface) exists between the solid and liquid phase. Displacement of the interface in one direction corresponds to solidification, and displacement in the opposite direction to melting. A system in which such a process occurs, has properties similar to those of a primary cell with very high internal resistance. Measurements were made of the short circuit current and the total charge separation. The first observations concerned dielectrics like carnauba wax, naphthalene (where the effect is particularly strong), and paraffin; however, occurrence in ice was also mentioned. Costa Ribeiro concluded that the effect was a general one: Production of currents and charge separation in dielectrics during phase changes. Later Workman and Reynolds[2] and Alfrey and Gill[3] found that orderly solidification of many aqueous solutions gives rise to the appearance of considerable open-circuit potentials (of the order of hundreds of volts) which become measurable when the freezing is observed inside a condenser in open circuit. These authors also give astonishingly high values for the total charge separation in aqueous solutions, and this was thought to be significant for the interpretation of atmospheric electricity. For this reason the effect, besides its theoretical interest, is likely to become of practical importance. Recently Krause and Renninger[4] found that individual crystals of pentaerythren become electrically charged during crystallization from a supersaturated solution. Numerous other papers have been published since 1944 on similar matters, partly in continuation of the previously mentioned ones,[5] partly independently.[6] It is also worth mentioning that as early as 1940 some observations along the same line were reported in meteorological papers.[7] It has already been asserted that the findings of Costa Ribeiro and Workman and Reynolds refer to the same effect[8] as does, in the author's opinion, the evidence contained in all previously mentioned papers. It is therefore justified to call

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[1] J. Costa Ribeiro, thesis, Universidade do Brasil, 1945; Anais acad. brasil. cienc. **17**, No. 2, 2, 3 (1945); **22**, 321 (1950).

[2] E. J. Workman and S. E. Reynolds, Phys. Rev. **74**, 709 (1948); **78**, 254 (1950).

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[5] J. Costa Ribeiro, Abstracts of Simposio sobre Novas Técnicas da Física, Rio de Janeiro, 1952 (unpublished), p. 23; L. Cintra do Prado, Anais acad. brasil. cienc. **18**, 145, 149 (1946); L. Cintra do Prado and P. Saraiva, Anais acad. brasil. cienc. **19**, 30 (1947); P. Saraiva, Anais acad. brasil. cienc. **18**, 161 (1946); A. Dias Travares, Anais acad. brasil. cienc. **25**, 53, 91 (1953).

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[7] W. Findeisen, Z. Meteorol. **57**, 6, 201 (1940); E. Lange, Z. Meteorol. **57**, 12, 429 (1940); A. Klumm, Arch. Meteorol., Geophys. u. Bioklimatol., Ser. **A3**, 382 (1951).

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the whole complex of phenomena with which we are here concerned the "thermodielectric effect," as it was called by its discoverer.

It has been mentioned by Costa Ribeiro that electrical phenomena occurring in the interface must be primarily responsible for the effect. However, an interface mechanism alone would not explain the production of voltages and currents in the external circuit. An additional mechanism is necessary to provide the macroscopic electric fields that force the charge carriers through the dielectric and raise the potential difference between the plates. This was found by Gill and Alfrey[3] in the production of space-charge distributions in the nonconducting (or at least badly conducting) solid phase. According to these authors, charge separation occurs primarily at the interface. Part of the charge produced there is, however, imprisoned in the ice, thus constituting a "frozen-in" space charge.[9] The charge carriers responsible are most likely the ions which are known to exist in considerable number in solid and liquid dielectrics unless they are purified to an extreme degree. Existing evidence about the influence of impurities on the effect corroborates this idea. However, in consequence of the rather general nature of the assumptions made, the pattern of the theory would not change basically if the carriers were electrons.

So far, no theory has been advanced that would allow correlation of the macroscopically observable quantities —current and voltage in the external circuit—with the potentials that must exist across the interface. In the present paper we shall attempt to do this, and shall show that available evidence about the behavior of ions in the dielectric and the structure of the interface leads one to expect the appearance of electrical effects during phase changes. The treatment is still approximate, applying only to "good" dielectrics such as were examined by Costa Ribeiro, in which the conductivity of the solid phase can be disregarded. The theory does not consider in detail the process of fusion or solidification, but is exclusively a "conductance" theory.

The basic mechanism is explained as follows. A contact potential difference—whether for ions or electrons makes no material difference—exists between the solid and the liquid. This contact PD results in the formation of a double layer at the interface under static conditions. If the interface moves, as in solidification or melting, the double layer would have to move with it. However, owing to the low conductivity of the solid site, the solid component of the charge cannot dissipate fast enough to keep up with the interface; hence, as the interface advances, it leaves behind a trail of space charge in the solid which builds up a potential difference between the region deep in the solid and the liquid (electrolyte) which can be many orders of magnitude larger than the contact PD. Thus the interface behaves like a selectively permeable membrane, allowing one kind of charge carrier to pass through more easily than the other, and "pushing along" with it a surface charge consisting of the excess charge left in the liquid. The combined fields of space and surface charges result in a counter emf at the interface which gradually neutralizes the contact PD, so that the trail of space charge decreases as the interface advances, and a limiting interface field is reached. The fraction of the double-layer charge which is actually left behind as space charge depends upon the velocity of advance of the interface and the rate at which charge is dissipated across the interface by back-diffusion. Mathematical formulation of these assumptions would lead directly to an expression for the conduction current across the interface corresponding to Eq. (15) and could be made the starting point for the theory.

In the present paper, however, a molecular model is introduced and the concept of a contact PD interpreted in terms of potential barriers and transition probabilities; rate theory is applied for obtaining the expression of the current through the interface. In this model the contact PD is shown to contain a term proportional to the speed of the phase change. This explains the experimentally found proportionality between equilibrium external current and speed of solidification or melting. But it must be emphasized that the simple analysis in terms of a contact PD, as outlined above, does not depend on such an explicit model; the mathematical restrictions introduced in the discussion for the sake of getting simple expressions are more severe than necessary for carrying out the calculations.

## I. MODEL OF INTERFACE

A condenser with plane plates contains a dielectric that is partly in the solid, partly in the liquid state. The phase boundary is assumed to run parallel to the surfaces of the electrodes. The conductance of the solid is supposed to be negligible, that of the liquid finite. The dielectric contains positive and negative ions, the relative concentration of which in the neutral state is the same. Thus no net charge exists under normal conditions. In the solid phase, as a consequence of the previously made assumptions of zero conductance, the ions are unable to move. In the liquid they can move more or less freely, having mobilities that depend on temperature and viscosity of the liquid. Thus conduction in the liquid can be described by the introduction of a specific conductance $\sigma$. In the interface the conductance changes from $\sigma$ to 0. It is just this zone that is of decisive importance.

Fröhlich[10] has applied rate theory to the problem of the movement of ions in solid dielectrics. He considers the existence of potential barriers which oppose the movement of ions within the dielectric. The probability of transition is given by a Boltzmann factor. Applying

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[9] See B. Gross and L. F. Denard, Phys. Rev. **67**, 253 (1945).

[10] H. Fröhlich, *Theory of Dielectrics* (Clarendon Press, Oxford, 1949).

this picture to the present case, we see that the potential barriers in the solid will have to be high to give sufficiently low conductance. In the liquid the barriers are practically absent. Then the phase boundary is characterized as a zone of finite extension where the height of the barriers decreases from its very high value inside the solid to its very low value inside the liquid. Within the interface the movement of the ions may be described in the way shown by Fröhlich.

The detailed picture of the interface is of no importance. It is sufficient to represent it schematically by a single potential barrier of finite height and the introduction of two potential minima on either side of the interface, one in the solid and the other in the liquid. The difference in the behavior of positive and negative ions in conducting dielectrics obliges one to assume that the height of the barrier and the energy difference between the minima are different for positive and negative ions. Thus one obtains Fig. 1 which gives the model of the interface used here. The height of the barrier at level I is $U_1^+$ for positive and $U_1^-$ for negative ions, and at level II it is, respectively, $U_2^+$ and $U_2^-$. The differences $U_1-U_2$ give the work functions. The levels running parallel to the phase boundary have an area $A$ and are separated by a distance $2d_0$. The surface densities of the ions in the levels are, respectively, $N_1^+/A$, $N_1^-/A$ and $N_2^+/A$, $N_2^-/A$. Probabilities of transitions from I to II and from II to I are, respectively, $w_{12}^+$, $w_{12}^-$ and $w_{21}^+$, $w_{21}^-$. The temperatures are $T_1$ and $T_2$.

The assumption of zero conductance in the solid makes it unnecessary to consider any transfer of ions to level I from the side of the solid. Thus the number of ions in I changes only by transport through the interface. It decreases by jumps from I to II and increases by jumps from II to I. Applying the equations of rate theory, one obtains

$$dN_1^+/dt = -w_{12}^+N_1^+ + w_{21}^+N_2^+, \tag{1a}$$

$$dN_1^-/dt = -w_{12}^-N_1^- + w_{21}^-N_2^-. \tag{1b}$$

If $e$ is the charge of the ions, then the conduction current across the interface is given by

$$i = e\frac{d}{dt}(N_1^+ - N_1^-). \tag{2}$$

The transition probabilities are given by

$$w = w_0 \exp(-U/kT), \tag{3}$$

where $U$ is the height of the potential barrier. In general, one has to consider the existence of an electrical field $E^*$ set up by the surface and space charges that build up in the system in consequence of the transport of ions through the interface. The presence of the field $E^*$ changes the height of a potential barrier from its value $U(0)$ without field to $U(0) \pm ed_0E^*$, the sign depending on the polarities of the ions and the direction of the jumps. Therefore,

$$U = U(0) \pm ed_0E^*. \tag{4}$$

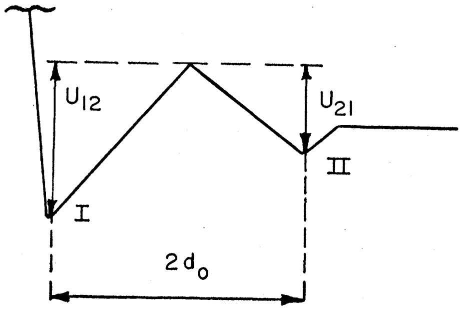

FIG. 1. Model of interface.

Finally, we expand Eq. (3) into a series and consider the first two terms only. This means linearization of the theory and therefore represents a considerable simplification for all following developments. We believe that within the framework of the present still semi-empirical theory this procedure is justified. (It could be made more rigorous by introducing the differences between the values $U^+$ and $U^-$ and expanding only the part containing them, but the final result would not differ significantly from the following.) Substituting (4) into (3) and designating the energy values without field by $U_1^+$, $U_1^-$, $U_2^+$, $U_2^-$ gives, finally

$$w_{12}^+ = w_0[1-(U_1^+ - ed_0E^*)/kT_1], \tag{5a}$$

$$w_{12}^- = w_0[1-(U_1^- + ed_0E^*)/kT_1], \tag{5b}$$

$$w_{21}^+ = w_0[1-(U_2^+ + ed_0E^*)/kT_2], \tag{5c}$$

$$w_{21}^- = w_0[1-(U_2^- - ed_0E^*)/kT_2]. \tag{5d}$$

Substituting (5) and (1) into (2) gives for the conduction current across the interface, the expression

$$\begin{aligned} i = ew_0[&\{(N_2^+ - N_2^-) - (N_1^+ - N_1^-)\} \\ &+ \{(N_1^+U_1^+ - N_1^-U_1^-)/kT_1 \\ &- (N_2^+U_2^+ - N_2^-U_2^-)/kT_2\} \\ &- ed_0E^*\{(N_1^+ + N_1^-)/kT_1 + (N_2^+ + N_2^-)/kT_2\}]. \end{aligned} \tag{6}$$

We now make the following two assumptions:

(a) The temperature gradient across the interface is very low, so that one can introduce the mean temperature

$$T = (T_1 + T_2)/2, \quad T_1 = T - \Delta T, \quad T_2 = T + \Delta T; \tag{7a}$$

(b) The difference in the number of positive and negative ions in each level is small compared with the total number of ions of each species. This is equivalent to saying that one has a rather small effect in a medium where under normal conditions the concentration of ions is relatively large. Under these conditions the values of $N_1$ and $N_2$ can be replaced by a mean value $N_0$ except in the first term of Eq. (6) which otherwise would cancel out. Introducing, furthermore, the coefficients

$$4H=(U_1{}^+-U_2{}^+)-(U_1{}^--U_2{}^-), \tag{8a}$$

$$4W=(U_1{}^++U_2{}^+)-(U_1{}^-+U_2{}^-), \tag{8b}$$

one obtains

$$i=ew_0\{(N_2{}^+-N_2{}^-)-(N_1{}^+-N_1{}^-)\}+\frac{4e^2w_0N_0d_0}{kT}\left\{\left(H+W\frac{\Delta T}{T}\right)\Big/ed_0-E^*\right\}. \tag{9}$$

## II. THE CONDUCTION CURRENT ACROSS THE INTERFACE

### a. The Electromotive Force

The primary cause of the current flow through the interface is the spontaneous jumping of the ions over the potential barrier. This mechanism is described by the term containing $H$ and $W$. It represents an electrochemical force. In Maxwell's theory one takes such forces into account by the introduction of an intrinsic electric field $E_0$. Applying this concept to the present case, one has

$$E_0=(H+W\Delta T/T)/ed_0. \tag{10}$$

The constant factor multiplying $E_0$ is an equivalent conductance of the interface. Thus,

$$\sigma_0=4e^2d_0w_0N_0/AkT. \tag{11}$$

The expression for the intrinsic field can be correlated with the speed of the phase change. Considering solidification, the experiment is conducted in such a way that one electrode is cooled while the other is kept at constant temperature. The heat exchange with the surroundings will be disregarded. Then heat is removed from the liquid across the interface only. The quantity of heat removed from the liquid per unit time is $-A\lambda\Delta T/2d_0$, where $\lambda$ is the coefficient of thermal conduction of the liquid and $\Delta T/2d_0$ is the temperature gradient. In consequence of the cooling, the mass of the liquid decreases per unit time by the amount $-cdm/dt$, where $c$ is the latent heat. Equalizing both quantities allows one to express the temperature gradient in terms of the amount of solidified material, giving

$$\Delta T=(2d_0c/A\lambda)dm/dt \tag{12}$$

and, therefore,

$$E_0=[H+W(2d_0c/A\lambda T)dm/dt]/ed_0. \tag{13}$$

The speed of the phase change $v$ is proportional to $dm/dt$. Therefore, $E_0$ consists of two components; one is constant and exists already under equilibrium conditions, the other appears only during phase changes and is directly proportional to the speed of the phase change. One can, therefore, write $E_0=c_1+c_2v$.

The current $J$, that in a shorted condition flows in the external circuit, will be proportional to $E_0$. Costa Ribeiro[5] has measured $J$ for various (constant) velocities of melting and solidification. He found that $J$ reaches an equilibrium value some time after the phase change has attained constant speed and that this equilibrium value is very nearly proportional to $dm/dt$. This suggests that the coefficient $c_1$ must be much smaller than $c_2$. Therefore a constant PD, independent of the temperature gradient, would not suffice to explain this result. The bulk of the intrinsic electromotive force must be due to the appearance of a temperature gradient across the interface. The introduction of the corresponding term in Eq. (10) was therefore relevant.

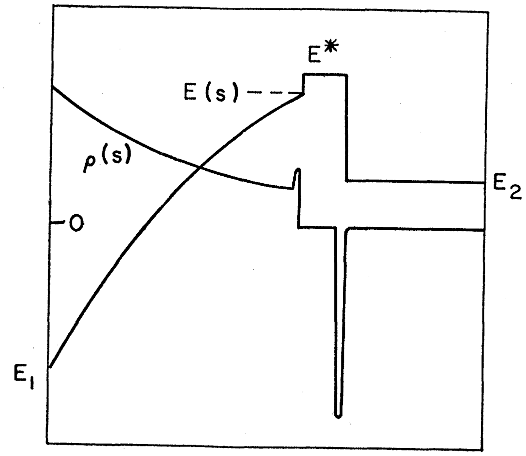

FIG. 2. Charges and field in dielectric.

### b. The Surface Charge

The term $e(N_2{}^+-N_2{}^-)/A$ is the density of the surface charge on level II and $e(N_1{}^+-N_1{}^-)/A$ the same for level I. Existence of a surface charge means discontinuity of the displacement field. Let $E(s)$ be the field in the solid adjacent to the interface, $E_2$ the field in the liquid, and $E^*$ the field in the interface (Fig. 2). Then

$$e(N_2{}^+-N_2{}^-)=A\epsilon(E_2-E^*),$$

$$e(N_1{}^+-N_1{}^-)=A\epsilon[E^*-E(s)],$$

and

$$e[(N_2{}^+-N_2{}^-)-(N_1{}^+-N_1{}^-)]=A\epsilon[E_2-2E^*+E(s)], \tag{14}$$

where $\epsilon$ is the dielectric constant of the system which for the sake of simplicity is taken to be the same for solid and liquid.

### c. The Current

Substituting (10), (11), and (14) into (9) gives

$$i=A\sigma_0(E_0-E^*)-Aw_0\epsilon[2E^*-E_2-E(s)]. \tag{15}$$

This equation has a direct physical significance. Consider again the distribution of fields and charges as shown in Fig. 2, the thickness of the solid deposit being $s$, electrode I being in contact with the solid, and electrode II being in contact with the liquid. The electric fields at the surfaces of the electrodes are, respectively, $E_1$ and $E_2$. According to previous assumptions, no space charge forms in the liquid; therefore, inside the liquid the field is constant and given everywhere by $E_2$. In the solid, space charge will exist. Therefore here the field is not in general constant, but varies from its boundary value $E_1$ at electrode I to the value $E(s)$ at a point close to the interface. Both sides of the interface carry surface charges of opposite sign. Therefore discontinuities of the field do appear. Inside the boundary layer, the field consists of the intrinsic field $E_0$ and the surface and space charge field $E^*$, the total field being $E_0-E^*$.

The mechanism of the interface current can now be described in the following way. Originally there exists an intrinsic field $E_0$. Starting from a neutral condition, this gives rise to an ionic current $\sigma_0 E_0$. In consequence, surface charges are set up at both sides of the interface and, eventually, space charges in the solid. The combined field of these charges is superposed on the intrinsic field and reduces the acting field in the interface from $E_0$ to $E_0-E^*$. The current produced falls off from its initial value $\sigma_0 E_0$ to $\sigma_0(E_0-E^*)$. Introducing the electromotive force $V_0=2d_0E_0$, the process can be thought of as a polarization phenomenon, with polarization voltage $V_p=2d_0E^*$. However, the accumulation of surface charge at both sides of the interface has still another consequence. This is the appearance of a back-current directly proportional to the differences in concentration of ions in the solid and the liquid, as given by the second term in Eq. (15). Like a diffusion current, it tends to equalize the ionic concentrations across the interface. Of course all terms are already implicitly contained in the fundamental equations. The electromotive force is associated with the existence of finite potential barriers and the thermal movement of the ions, the polarization with changes in the height of the potential barriers by the field, and the diffusion current with the proportionality between the number of jumps and concentration of ions in each potential minimum. The linearity of the expression follows from the series expansion of the Boltzmann factor. The fields $E_1$ and $E_2$ are functions of time, and the field $E(s)$ is a function of time and distance. Therefore, $i$ is a function of $t$ and $s$ and has to be written $i(t,s)$.

Equation (15) contains both the field $E^*$ inside the boundary layer and the field $E(s,t)$ in the solid adjacent to the interface. In the present case one can, however, neglect the difference between both fields. During solidification a continuous flow of current $i$ goes through the interface. After the interface has advanced a certain distance, say $a$, an excess charge $q_a$ is found in the solid and an excess charge of the same amount, but contrary polarity, is found in the liquid. However, while in the solid the charge is distributed over the distance $a$ in the form of a space charge, in the liquid it constitutes a surface charge adhering to the interface. It becomes therefore understandable, that the value of the surface charge at the solid site can be disregarded. With this assumption, the discontinuity of the field at the solid site disappears and $E(s,t)$ becomes identical with $E^*$. Of course, this consideration is valid only for processes involving phase changes.

Putting, therefore, $E^*=E(s,t)$, Eq. (15) transforms into

$$i=A\sigma_0[E_0-E(s,t)]-Aw_0\epsilon[E(s,t)-E_2(t)]. \quad (16)$$

### d. The Space Charge

The total amount of charge carried across the interface in time $dt$ is $dq=idt$. With the interface in a fixed position, the result of the charge transfer would be only the formation of an electric double layer. Here, however, we are interested in phase transitions where the interface advances with velocity $v=ds/dt$. To cover the distance $ds$, the interface needs the time $dt=ds/v$. The charge transferred through the interface while the latter has advanced by $ds$, is, therefore,

$$dq=ids/v. \quad (17)$$

This charge, however, does not any longer constitute a surface charge, but is distributed over $ds$ and constitutes a space charge. The assumption of zero conduction for the solid makes consideration of charge decay unnecessary. The density of space charge is

$$\rho=\frac{1}{A}\frac{dq}{ds}, \quad (18a)$$

or

$$\rho=i/Av, \quad (18b)$$

with $i$ given by (16). Poisson's equation for the field in the solid at a point close to the interface then is

$$\epsilon\partial E(s,t)/\partial s=i(s,t)/Av(t). \quad (19)$$

## III. THE SPACE-CHARGE FIELD

The value of the current in (19) must now be replaced by its explicit expression (16). We assume that the phase change proceeds with constant speed $v=$ constant. Then, making the substitutions, one gets finally

$$\frac{\partial E(s,t)}{\partial s}+\frac{E(s,t)}{s_0}=\frac{E_0+kE_2(t)}{s_0(1+k)}, \quad (20)$$

with

$$1/s_0=(1+k)\sigma_0/\epsilon v, \quad (21a)$$

and

$$k=\epsilon w_0/\sigma_0. \quad (21b)$$

This equation must be integrated with the initial condition

$$s=0\colon\; E(0,t)=E_1(t). \quad (22)$$

The solution is given by

$$E(s,t)=\frac{E_0+kE_2(t)}{1+k}-\left\{\frac{E_0+kE_2(t)}{1+k}-E_1(t)\right\}e^{-s/s_0}. \quad (23)$$

Integrating once more between 0 and $x$, one obtains the space-charge potential $V(x,t)$ at time $t$ and the point $x$, where the interface is found at that time; that is,

$$x=vt. \tag{24}$$

This gives

$$V(x,t)=x\frac{E_0+kE_2(t)}{1+k}-s_0\left(\frac{E_0+kE_2(t)}{1+k}-E_1(t)\right)(1-e^{-x/s_0}), \tag{25}$$

or, substituting $x$ from (24),

$$V(t,t)=vt\frac{E_0+kE_2(t)}{1+k}-vt_0\left(\frac{E_0+kE_2(t)}{1+k}-E_1(t)\right)(1-e^{-t/t_0}), \tag{26}$$

where

$$t_0=\epsilon/\sigma_0(1+k). \tag{27}$$

## IV. THE DIFFERENTIAL EQUATIONS FOR CURRENT AND VOLTAGE

We are now in a position to establish the equations for the observable quantities, i.e., currents and voltages in the external circuit, under different conditions of the experiment. Let $U(t)$ be the total potential difference between the plates, $D$ the distance between the plates, and $J(t)$ the external current.

The total current must be the same in the solid and the liquid. In the latter it contains a conduction and a displacement component, in the former it is purely displacement current. Writing the equations for the surfaces of both electrodes gives

$$J(t)=A\epsilon dE_1(t)/dt, \tag{28a}$$

$$J(t)=A\epsilon dE_2(t)/dt+A\sigma E_2(t), \tag{28b}$$

and, therefore,

$$\epsilon dE_1(t)/dt=\epsilon dE_2(t)/dt+\sigma E_2(t). \tag{29}$$

This is the differential equation connecting the field values at the two electrodes.

The total voltage drop across the plates is constituted by the space charge potential in the solid, the potential drop across the interface, and the voltage loss in the liquid. Disregarding the voltage drop across the interface, this gives

$$U(t)=V(t,t)+(D-x)E_2(t). \tag{30}$$

Equations (26), (29), and (30) together constitute a system that permits determination of $E_1$, $E_2$, and $J$. Different experiments are characterized by different boundary conditions. For the measurement of the short circuit current one has $U(t)=0$; for the measurement of the open circuit voltage one has $J(t)=0$.

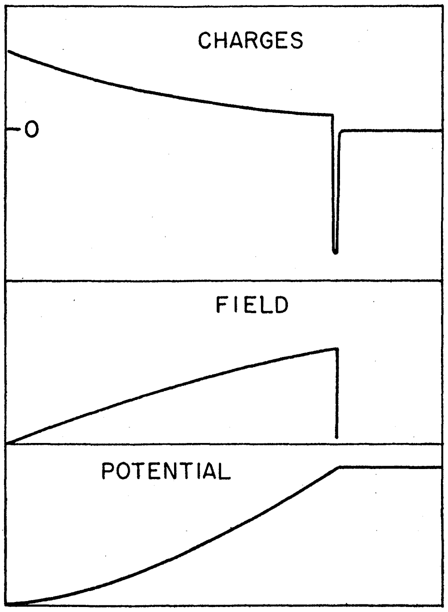

FIG. 3. Open-circuit behavior.

## V. OPEN-CIRCUIT VOLTAGE

We shall give here only the calculation of the open-circuit voltage as it would be measured by an electrometer of negligible capacitance. From the condition

$$J(t)=0 \tag{31}$$

it follows that both $E_1(t)$ and $E_2(t)$ are equal to 0. The absence of a voltage drop in the liquid makes the measured potential difference equal to the space charge potential. From (26) one gets

$$U(t)=\frac{vE_0}{1+k}\{t-t_0(1-e^{-t/t_0})\}. \tag{32}$$

Expanding for small and large values of $t/t_0$ gives

$$t/t_0\ll 1:\quad U(t)=\frac{vt_0E_0}{2(1+k)}(t/t_0)^2, \tag{33a}$$

$$t/t_0\gg 1:\quad U(t)=vE_0t/(1+k). \tag{33b}$$

The voltage increases at first quadratically, later linearly. The maximum voltage reached when the entire system has solidified is approximately equal to $DE_0/(1+k)$. The ratio of the maximum open-circuit voltage to the interfacial potential is therefore $D/2d_0(1+k)$. This shows that the external voltage can exceed the electromotive force by a great amount, provided $k$ is not exceedingly high. The space charge mechanism then represents a voltage amplification system. Supposing for dimensional reasons that $k$ is of the order of 1, and taking the thickness of the interface as equal to $10^{-6}$ cm, gives for a 1-cm cell a total voltage of about 50 v, as corresponding to an electromotive force $E_0$ equal to $\frac{1}{10}$ of a millivolt. A comparison with the measurements of Workman and Reynolds is unfortunately not possible because in their case the assumption of zero conduction for the solid does not hold. However, it is gratifying to see that a mechanism of the type considered here can cause the appearance of the potential differences, and generally of the effects of the kind found by the observers.

In the present case (open circuit) the total amount of surface charge in the liquid adhering to the interface is equal to the total amount of space charge, the entire system remaining neutral. The space charge distribution in the solid is exponential (see Fig. 3). According to (23), the field is given by

$$E(s)=E_0(1-e^{-s/s_0})/(1+k),\quad s\leq x \tag{34}$$

and

$$\rho(s)=\epsilon E_0 e^{-s/s_0}/s_0(1+k),\quad s\leq x. \tag{35}$$

The voltage is at any time proportional to $vE_0$. Since we found $E_0=c_1+c_2v$, one has

$$U(t)=(c_1v+c_2v^2)f(t). \tag{36}$$

Thus voltage curves obtained with different speeds of phase change differ only by a factor lying roughly between $v$ and $v^2$.

## VI. CONCLUSIONS

The foregoing exposition shows that a relatively simple theory based on existing evidence about interface potentials and behavior of ions in dielectrics can account for charge separation, and the production of voltages and currents during phase changes. The theory leads to expressions for the space-charge distribution in the solid and the voltage-time curves in open circuit that eventually may be compared with experimental data. The differential equation for the short-circuit current can be obtained in a straightforward manner; it is omitted here because it is not easily integrated. In the present form the theory is still incomplete. Among the factors it does not take into account are (a) the conductivity of the solid that affects the reversibility of the effect and the form of the voltage-time curves in aqueous solutions, and (b) the diffusion of ions in the liquid that may also play a rôle when a solid dielectric is dissolved in a solvent. However, we believe that the theory describes correctly the principal mechanism of interface conduction and presents already the basis for a more precise and complete treatment.

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# Stored Energy Measurements in Irradiated Copper

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Thin copper foils, cooled to liquid nitrogen temperature, were subjected to bombardment by 12-Mev deuterons. The stored energy released due to annealing of the radiation damage was measured as the foils warmed to room temperature. Below −40°C the stored energy released per °C was approximately uniform and is presumed to result from annihilation of closely spaced interstitial-vacancy pairs produced by the bombardment. A prominent maximum in the annealing spectrum occured at −15°C and is interpreted as binary recombination of interstitial atoms and vacancies by means of interstitial diffusion. Changes in residual electrical resistivity were also measured. The stored energy to resistivity ratio was found to be $1.7\pm0.2$ cal/gram per micro-ohm-cm, both for the low-temperature processes and the −15°C annealing peak. If the energy of formation of an interstitial-vacancy pair is 5 ev, a value of 11 micro-ohm-cm for the resistivity of one atomic percent of pairs is obtained. The atomic concentration of interstitial atoms and vacancies produced by an irradiation of $10^{17}$ deuterons/cm$^2$ at liquid nitrogen temperature is, accordingly, $5\times10^{-5}$.

## I. INTRODUCTION

CHANGES in the physical properties of a metal resulting from irradiation with fast particles are difficult to interpret because the types and numbers of imperfections produced by the bombardment are unknown. Interstitial atoms and vacant lattice sites are expected[1] to be the predominant types produced, and this view is supported by the observed annealing properties[2] of the damage. The resulting decrease in electrical resistivity upon anneal has received the greatest amount of experimental study, but the inherent difficulties of corresponding theoretical calculations have prevented a determination of the number of interstitial-vacancy pairs that occur.

The measurement of a fundamental quantity, such as energy, should provide a more reliable method of

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