Static Space-Charge Effects in the Diffuse Double Layer

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(Received December 2, 1953)

Exact solutions of the static Debye-Hückel space-charge equations for one and for two blocking electrodes are compared analytically and graphically. It is found that the simpler one-electrode solution may be employed to characterize the diffuse double layer with high accuracy in most experimental situations in place of the less tractable two-electrode solution which involves Jacobian elliptic functions. Some consequences of the strong nonlinear voltage dependence of the exact solutions are considered and the application of the solutions to physical situations is discussed.

INTRODUCTION

THE treatment of space-charge formation problems in solids, liquids, and gases involves the solution of systems of nonlinear partial differential equations. These equations have never been solved exactly in complete generality, but a number of exact solutions have been obtained for specific limiting cases. Thus, Jaffé[1] has obtained an exact solution for the one-dimensional, static space-charge distribution in a material containing univalent free positive and negative charges without recombination for the case of two blocking (polarized), plane parallel electrodes separated by a distance L. Unfortunately, this solution involves Jacobian elliptic functions and, because of the inadequacy of published tables of these functions, is difficult to use in practice.

Recently, Prim[2] has solved the same problem anew but with different boundary conditions. Prim considers an intrinsic semiconductor region bounded by n- and by p-type extrinsic regions. The junctions between extrinsic and intrinsic regions are not, therefore, blocking in this case, but the solution is of the same form as Jaffé's.

The solution of the space-charge equations in the time-varying case is immeasurably more difficult than their solution in the static case. Recently, Keilson[3] has given an exact solution for the time variation of injected carriers in semiconductors, but the exact dependence of carrier concentration on position is not obtained. Jaffé and LeMay[4] have given an approximate solution for the time-dependent charging current pertaining to the one-dimensional problem involving two blocking electrodes separated by a distance L to which a dc voltage is suddenly applied. Also, the author[5] has published a linearized theory of space-charge effects for ac applied voltages in the case of two blocking electrodes for any degree of dissociation and for any ratio of the mobilities of positive and negative carriers.

In the preceding paper,[6] the author and M. K. Brachman discussed an exact solution to the static diffuse-double-layer problem where only one plane parallel blocking electrode is present at the boundary of a material of semi-infinite extent containing mobile free charges of both signs. This solution is of particular interest because it involves only the usual well-tabulated elementary transcendental functions. Since both this solution and that of Jaffé for two electrodes are exact, they show clearly the nonlinear dependence of space-charge concentration, space-charge capacitance, etc., on the applied voltage. In this paper, the two solutions are first compared in order to indicate in what physical situations the simpler transcendental solution may be employed in place of the more complicated elliptic solution. Then, some of the implications of the great nonlinearity of the solutions are discussed and application of the solutions to physical situations considered.

EXACT STATIC SOLUTIONS FOR THE DIFFUSE DOUBLE LAYER

Diffuse double-layer formation in the physical situation involving a blocking anode at $x=0$ and an infinite extent of material containing free charges in the positive x direction was considered in the preceding paper.[6] The free charges are assumed univalent and do not recombine. A dc potential V_0 is applied between the anode and the cathode at infinity and the zero of potential is taken at the cathode. The results obtained in II for this situation may be summarized as follows

$$\psi^* \equiv \psi/(kT/e) = \ln\{\coth^2\tfrac{1}{2}[x/L_D + \sinh^{-1}(\operatorname{csch}\tfrac{1}{2}V_0^*)]\} \tag{1}$$

$$n^* \equiv n/c_0 = c_0/p \equiv 1/p^* = \exp(\psi^*) \tag{2}$$

$$\mathcal{E}^* \equiv \mathcal{E}/(kT/eL_D) = 2\operatorname{csch}\{x/L_D + \operatorname{csch}^{-1}(\sinh\tfrac{1}{2}V_0^*)\}. \tag{3}$$

In these equations, ψ is the potential within the material, n is the concentration of negative charge carriers, p the concentration of positive carriers, and $\mathcal{E}$ the electric field strength. The quantity c_0 is the common,

[1] G. Jaffé, Ann. Physik **16**, 217 (1933).
[2] R. C. Prim, Bell System Tech. J. **32**, 665 (1953).
[3] J. Keilson, J. Appl. Phys. **24**, 1198 (1953).
[4] G. Jaffé and C. Z. LeMay, J. Chem. Phys. **21**, 920 (1953).
[5] J. R. Macdonald, Phys. Rev. **92**, 4 (1953).
[6] J. R. Macdonald and M. K. Brachman, J. Chem. Phys. **22**, 1314 (1954). We shall, in the present work, refer to this paper as II and that of reference 5 as I.

homogeneous, equilibrium value of n and p before the application of V_0; V_0^* is $V_0/(kT/e)$; and L_D is given by

$$L_D = [\epsilon kT/8\pi e^2 c_0]^{\frac{1}{2}}, \tag{4}$$

where ϵ is the dielectric constant of the material in the absence of free carriers.

Next, let us consider the case of a blocking anode at $x=0$ and a blocking cathode at $x=L$. Expressed in terms of the variable $y=(x/L_D-L/2L_D)$, Jaffé's exact results for this problem[1] are

$$\psi^* = \ln\{(dny-k_1 sny)/(dny+k_1 sny)\} \tag{5}$$

$$n^* = 1/p^* = \exp(\psi^*) \tag{6}$$

$$\mathcal{E}^*(y) = 2k_1/cny. \tag{7}$$

Here,

$$k_1 = \{cnM/snM\}\sinh(V_0^*/4), \tag{8}$$

and

$$dnM/cnM = \cosh(V_0^*/4). \tag{9}$$

The quantity M is the dimensionless constant $L/2L_D$. Equation (9) was not given by Jaffé but follows from his work and is useful in simplifying the exact formulas in specific cases. The zero of potential is taken at $x=L/2$. The above exact solution only applies to the case $\mathcal{E}^*(0) \leqslant 2$. This condition is usually well satisfied
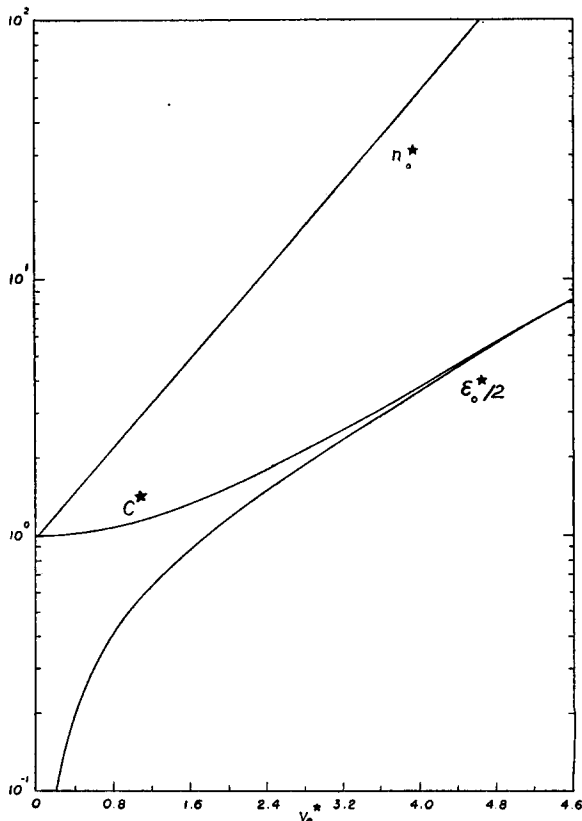

FIG. 1. Dependence on normalized voltage $V_0^* = V_0/(kT/e)$ of normalized carrier concentration n_0^* and electric field strength $\mathcal{E}_0^*$ at the surface of a blocking electrode for single-electrode case. The normalized layer capacitance C^* is also shown.

in cases of practical interest. Jaffé also gives exact solutions for $\mathcal{E}^*(0)=2$ and $\mathcal{E}^*(0) \geqslant 2$, but we need not consider them in this paper.

In most cases of interest, M will be greater than five. When M is this large or larger, k_1 will be much smaller than unity for any value of V_0^*. The Jacobian elliptic functions dn, cn, and sn are functions of both their argument y or M and of k_1. Thus, Eq. (8) is actually a transcendental equation for k_1. For $k_1 \ll 1$, no tables of these functions are available. In order to compare the predictions of Eqs. (5), (6), and (7) with those of (1), (2), and (3), it is therefore necessary to use approximate expressions for the elliptic functions which apply in the case $k_1 \ll 1$. These expressions are

$$sny = \tanh y + (k_1^2/4) \operatorname{sech}^2 y(\sinh y \cosh y - y) \tag{10}$$

and

$$cny = [1 - (k_1^2/4) \tanh y(\sinh y \cosh y - y)] \operatorname{sech} y. \tag{11}$$

The function dny may be calculated using (10) and (11) from the exact relation

$$dny = [(cny)^2 + k_1^2(sny)^2]^{\frac{1}{2}}. \tag{12}$$

When y is greater than about three, the final y terms in (10) and (11) may be neglected with little loss of accuracy.

If expressions of the form (10) and (11) are substituted in Eq. (8) for k_1, a cubic equation in k_1 is obtained. The cubic term is many orders of magnitude smaller than the other terms for $k_1 \ll 1$ and may be neglected. The exact solution of the resulting quadratic equation for k_1 is

$$k_1 = 2 \operatorname{csch} M \tanh(V_0^*/8). \tag{13}$$

This equation is a good approximation so long as the value of k_1 computed from it is less than about $1/20$. This expression for k_1 is considerably different from that given by Jaffé[1] for the same case of large M. Furthermore, it leads to quite different y dependence for ψ^* and $\mathcal{E}^*$ than that obtained by Jaffé. The difference arises from the inclusion in the present work of the $k_1^2/4$ terms in the approximate expressions (10) and (11), in contrast to their neglect by Jaffé. Such neglect is permissible in the expression for sny but is a poor approximation for the cny expression. The inclusion of these terms in the present work thus gives more accurate final approximate expressions for k_1 and for ψ^* and $\mathcal{E}^*$.

Before comparing the two dc space-charge solutions graphically, it is of interest to compute the space-charge capacitance represented by the concentration of charge near the electrode(s). Let a subscript zero denote the value of a quantity at $x=0$. Then the total differential capacitance[7] is

$$C_T{}^d = -\partial \sigma_0/\partial V_0 = (\epsilon/4\pi)(\partial \mathcal{E}_0/\partial V_0), \tag{14}$$

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[7] All results apply to unit area of the system.

and the less important static capacitance is simply $-\sigma_0/V_0$, where σ_0 is the surface charge density in the material at the electrode. Using expression (3) for $\mathcal{E}^*$, we obtain for the differential capacitance

$$C_T{}^d = (\epsilon/4\pi L_D)\,\cosh(V_0{}^*/2) \qquad (15)$$

in the one-electrode case. In the two-electrode case, it follows from Eqs. (7) and (8) that

$$\mathcal{E}_0{}^* = 2(snM)^{-1}\sinh(V_0{}^*/4). \qquad (16)$$

Using the approximate expression (11) for snM with neglect of the small $k_1{}^2/4$ term, we obtain

$$\mathcal{E}_0 \cong (2kT/eL_D)\,\coth M \,\sinh(V_0{}^*/4). \qquad (17)$$

Thus, we find for $C_T{}^d$

$$\begin{aligned}C_T{}^d &= (\epsilon/4\pi L_D)\tfrac{1}{2}\,\coth M \,\cosh(V_0{}^*/4)\\ &= C_g M \,\coth M \,\cosh(V_0{}^*/4).\end{aligned} \qquad (18)$$

This expression represents the total capacitance of the two space-charge layers in series, in parallel with the geometrical capacitance of the material, $C_g = \epsilon/4\pi L$. In the one-electrode case, there was only one space-charge layer and no geometrical capacitance, since L was infinite in this case. The space-charge capacitance for both layers in series in the present case is given by $C_s{}^d = (C_T{}^d - C_g)$ and may be written

$$C_s{}^d = C_g[M\,\coth M\,\cosh(V_0{}^*/4)-1]. \qquad (19)$$

For comparison with Eq. (15), the space-charge capacitance of a single layer is $2C_s$. For large M or V^*, the C_g correction is negligible and $2C_s{}^d(\equiv C_{s1}{}^d)$ becomes

$$C_{s1}{}^d \cong (\epsilon/4\pi L_D)\,\coth M\,\cosh(V_0{}^*/4). \qquad (20)$$

This expression differs from that of (15) by the factor $\coth M$ which is essentially unity for $M>3$ and by the appearance of $V_0{}^*/4$ in place of $V_0{}^*/2$.

It is worth noting that the linearized, small-signal theory of ac space-charge effects presented in I yields for positive and negative carriers of nonzero mobility an expression for low-frequency limiting capacitance C in the two-electrode case of exactly the form (19) but with $\cosh(V_0{}^*/4)$ replaced by unity. The present solution shows under what conditions the earlier solution for C is valid. Of course in a linear solution there is no difference between the static and differential capacitances.

COMPARISON OF EXACT STATIC SOLUTIONS FOR THE DIFFUSE DOUBLE LAYER

We are now in a position to compare the predictions of the two exact space-charge solutions. Before comparing the solutions graphically, valuable conclusions may be drawn from comparison of the analytical expressions at $x=0$. In the one-electrode case, $\psi^* = V_0{}^*$ at $x=0$; thus $n_0{}^* = \exp(V_0{}^*)$, $\mathcal{E}_0{}^* = 2\sinh(V_0{}^*/2)$. For the two-electrode case, on the other hand, $\psi^* = V_0{}^*/2$ at $x=0$, and $n_0{}^* = \exp(V_0{}^*/2)$, $\mathcal{E}_0{}^* = 2(snM)^{-1}\sinh(V_0{}^*/4)$. The principal difference in these expressions lies in the
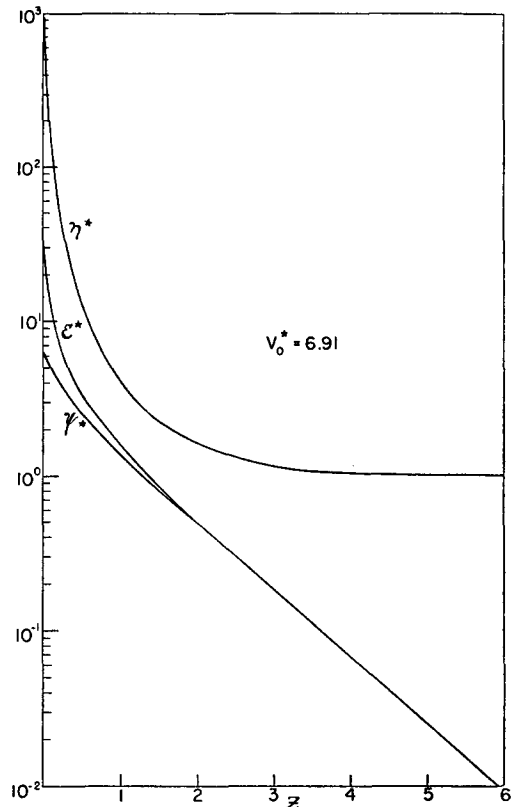

FIG. 2. Dependence for one-electrode case of n^*, $\mathcal{E}^*$, and normalized potential ψ^* on distance from blocking anode in Debye-length units for $V_0{}^*=6.91$.

substitution of $V_0{}^*/2$ for $V_0{}^*$ when passing from the one to the two-electrode case. This result is physically plausible because in the two-electrode case one would expect that half the applied voltage drop would occur near each of the two space-charge layers. Since there is only one layer in the one-electrode case, the full voltage drop occurs in this layer.

Figure 1 shows how the quantities $n_0{}^*$, C^*, and $\mathcal{E}_0{}^*$ depend on $V_0{}^*$ for the one-electrode case. Here $C^* = C_T{}^d/(\epsilon/4\pi L_D)$. This graph also closely gives the dependence of $n_0{}^*$ and $\mathcal{E}_0{}^*$ on $V_0{}^*$ in the two-electrode case if the abscissa is taken as $2V_0{}^*$ instead of $V_0{}^*$. The presence of the term $(SnM)^{-1}$ in the two-electrode expression for $\mathcal{E}_0{}^*$ may be neglected because this term is very close to unity. The C^* curve represents $C_{s1}{}^d$ (see Eq. 20) closely since $\coth M$ will also be essentially unity for $M \geqslant 3$.

Figure 2 shows the dependence of n^*, $\mathcal{E}^*$, and ψ^* on position measured from the blocking electrode for the one-electrode case. The value of $V_0{}^*$ is selected to make $n_0{}^* = 10^3$. At room temperature, this corresponds to an applied voltage of only about 0.18 volt. Thus, only very small voltages are required to establish very inhomogeneous space-charge distributions. Since this is a semilogarithmic plot, the linear decay of $\mathcal{E}^*$ and ψ^* for $z \equiv x/L_D > 1.5$ implies that these quantities depend exponentially on z in this range.
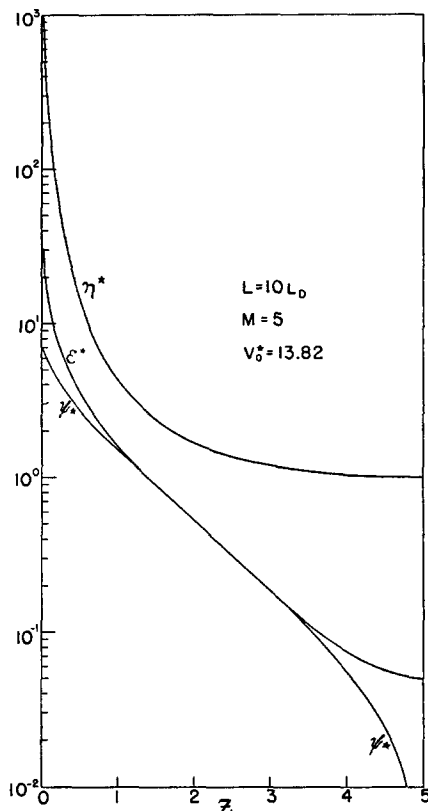
FIG. 3. Dependence for two-electrode case of n^*, $\mathcal{E}^*$, and ψ^* on distance from blocking anode at $x=0$ in Debye-length units for $V_0^*=13.82$ and $M=L/2L_D=5$.

Figure 3 is similar to Fig. 2 except it is for the two-electrode case with $M=5$. The dependence of n^*, $\mathcal{E}^*$, and ψ^* is plotted for only half the separation between electrodes. n^* and ψ^* are odd functions about the center line; $\mathcal{E}^*$ is an even function. It will be noted that the curves of Fig. 3 are plotted for twice the value of V_0^* used in Fig. 2. Half of the voltage drop should take place between $x=0$ and $x=5L_D(z=5)$ and the other half from $5L_D$ to $10L_D(=L)$. Thus, by using twice the value of V_0^* as that used in Fig. 2, we ensure that the space-charge layer near $x=0$ in Fig. 3 for the two-electrode case will have the same voltage applied across it as the single layer in the one-electrode case. We are thus enabled to compare the two cases directly.

Comparison of the curves of Figs. 2 and 3 for $0 \leqslant z \leqslant 5$ shows very close agreement. For z less than about 3.3, the eye is unable to distinguish any difference in the respective curves when they are centered over one another. For $3.3 < z \leqslant 5$, the influence of the finite separation of electrodes in the two-electrode case becomes apparent. In this case, n^* must reach unity at $z=5$, whereas unity is not reached in the one-electrode case until $z= \infty$. Nevertheless, the difference in the entire n^* curves in the common region is difficult to detect by eye and is essentially negligible. The

distinction shows up more clearly in the $\mathcal{E}^*$ and ψ^* curves in the region $3.3 < z \leqslant 5$. For example, at $z=5$, $\mathcal{E}^*$ is 0.05 in the two-electrode case and 0.025 in the one-electrode case. ψ is the quantity most accessible to measurement, however. The distinction between the two ψ curves would be difficult to establish experimentally because in the region where the difference appears, the potential will have fallen to values much smaller than the applied voltage.

The foregoing discussion indicates that for $M \geqslant 5$ the simpler one-electrode solution is sufficiently accurate in the two-electrode case for practically all cases. To use the one-electrode solution for this purpose, one-half of the potential V_0 applied between the two electrodes is used in the one-electrode equations. In most cases of experimental interest there will indeed be two electrodes separated by a distance L, but M will usually be far greater than 5. The larger the value of M, the closer will the two solutions coincide over their common region. In the exceptional cases when $M < 5$, Jaffé's exact solutions for $\mathcal{E}_0^* \geqslant 2$ may be used together with the approximate expressions (10) and (11). Note that if one of the two electrodes is not blocking but ohmic, the one-electrode solution will apply very closely with the entire applied voltage drop occurring across the single space-charge layer at the blocking electrode.

DISCUSSION OF VOLTAGE-DEPENDENT NONLINEARITY FOR THE DIFFUSE DOUBLE LAYER

We shall now restrict attention to the consequences of the voltage-dependent nonlinearity of the one-electrode solution as shown graphically in Fig. 1. Table I shows how rapidly some of the pertinent space-charge quantities increase with applied voltage. The last column gives the electric field strength at the blocking electrode for a typical Debye length of 10^{-5} cm. These results indicate clearly that the exact solution must fail for various reasons for some voltage between 0.1 and 3 volts. For example, the solution gives a value of n_0^* which exceeds the number of conduction band levels available at $x=0$ for a voltage of the order of one volt.

Even before these limits are reached, the solution will fail because of dielectric saturation, which decreases the dielectric constant in the high-field region near the electrode, and because of high-field emission from the electrode itself. Such failure will occur between 10^{-1} and 1 volt for $L_D=10^{-5}$ cm as shown by the high values of $\mathcal{E}_0$ in Table I in this voltage range. It should be especially noted that if the electrode is not completely blocking for all charge carriers, the field will not be by any means so large as that specified by the present solution with complete blocking. For example, Von Hippel, Gross, Jelatis, and Geller[8] have given an approximate solution for the field at a rectifying

[8] Von Hippel, Gross, Jelatis, and Geller, Phys. Rev. 91, 568 (1953).

electrode with the neglect of diffusion. These authors treat the case of two rectifying electrodes back-to-back so that charges may leave through the electrodes but may not enter, and find a square root dependence of $\mathcal{E}_0$ on applied voltage rather than the present essentially exponential dependence. The reason for the difference is that in the rectifying case charges will be entirely withdrawn from the material at one electrode until an exhaustion layer forms at the other electrode. The space-charge density in the exhaustion layer is limited by the donor (or acceptor) concentration originally present and hence cannot rise to the astronomical values to which the mathematical solution for n_0^* leads in the blocking, one-electrode case. In practical cases, of course, dielectric saturation and high-field emission will limit the exponential increase to a maximum value in the blocking-electrode case also.

The dependence of the space-charge-layer differential capacitance on $\cosh(V_0^*/2)$ is of considerable interest. The foregoing discussion indicates that the observed capacitance arising from space charge may be expected to increase from a constant small-signal value up to a value ten or more times greater before breakdown limits the increase. Such voltage dependence might be of considerable value for such applications as dielectric amplifiers if it could be attained in practice.

APPLICATION TO PHYSICAL SITUATIONS

Both the Jaffé[1] and the Müller-Macdonald-Brachman[6] solutions apply to the situation where mobile, univalent, noncombining charges of both signs are present. This is the case, for example, in strong electrolytes, which are completely dissociated. In weak electrolytes, dissociation is incomplete and recombination must be taken into account. If bimolecular recombination terms are added to the Debye-Hückel differential equations which govern the space-charge distribution, the equations become even more nonlinear and, apparently, cannot be solved exactly in closed form. The linearized solution of the author[5] with the ac frequency taken zero applies to this case, however, for very small applied voltages ($V_0^* \ll 1$). When V_0^* is no longer small compared to unity, neither the linearized solution nor either of the present nonlinear solutions apply. Of course, in this case, the

nonlinear solutions will be better approximations to the exact solution.

Another case of considerable physical interest is that where charges of only one sign are mobile. An insulator containing donors such as the F centers in alkali-halide crystals is an example. Also, a semiconductor containing a fairly high concentration of donors or acceptors may represent this situation provided that the carriers originating from donors or acceptors are present in much higher concentration than are the intrinsic carriers. If the mobile carriers can recombine, no matter how infrequently, with the immobile charges of opposite sign (e.g., donor ions), it is easy to show that the final static space-charge distribution is specified exactly by either the Jaffé or the Müller-Macdonald-Brachman solution as the case may be, provided that the ionized donor concentration predicted by theory never exceeds the total neutral donor concentration originally present at any point. Effectively, charges of both sign are mobile because the release of a mobile charge at one position in the material and its capture by a center of opposite sign at another position represents an actual transfer of an immobile charged center from one position to the other. If recombination is very infrequent, a long time will be required before the space-charge distribution will be close to that represented by the exact solution; nevertheless, the exact solution will eventually apply. If we denote by L_{D1} and L_{D2} the Debye lengths corresponding to univalent mobile carriers of only one sign and to mobile carriers of both signs, respectively, then $\sqrt{2}L_{D1} = 2L_{D2}$. When one is dealing with mobile, recombining charges of a single sign, M may be equivalently given as $L/\sqrt{2}L_{D1}$ in all the preceding equations. Note that $\sqrt{2}L_{D1}$ is the rms Debye length for a single carrier.

When charges of only one sign are mobile but there is no recombination (infinite recombination time), there is no way for the immobile charges of opposite sign to move and they will not, therefore, contribute to the space charge. Unfortunately, the Debye-Hückel equations pertaining to this case cannot, apparently, be solved exactly in terms of closed functions for either the one-electrode or the two-electrode case. The linearized solution of I shows that $M = L/2L_{D1}$ here as would be expected. However, the nonlinear voltage dependence required by the nonlinearity of the differential equations does not appear in this solution. It is possible to obtain a series solution to the differential equations by means of the reversion method,[9] first employed by Helmholtz. Unfortunately, in the case of most interest, for which the nonlinearity is appreciable and $V_0^* \gtrsim 1$, the convergence of the series is too slow to make the solution practical. A physical situation where charges of a single sign only are mobile and where there is absolutely no recombination is unlikely. On

TABLE I. Voltage dependence of various space-charge quantities at room temperature.

V_0 (volts)	V_0^*	n_0^*	$\mathcal{E}_0^*$	C^*	$\mathcal{E}_0$ for $L_D = 10^{-5}$ cm (volt/cm)
10^{-2}	0.385	1.47	0.388	1.02	1.0×10^3
0.0316	1.22	3.39	1.298	1.19	3.4×10^3
10^{-1}	3.85	47.0	6.74	3.52	1.8×10^4
0.316	12.2	2×10^5	446	223	1.2×10^6
1	38.5	5×10^{16}	2.2×10^8	1.1×10^8	6×10^{11}
3.16	122	1×10^{53}	3×10^{26}	1.5×10^{26}	8×10^{29}

[9] G. I. Cohn and B. Saltzberg, J. Appl. Phys. 24, 180 (1953).

the other hand, if the recombination time is very long, an initial space-charge distribution involving the mobile charges only may be established long before recombination can effectively mobilize the immobile charges of opposite sign so that they can contribute to the space-charge distribution. The final static distribution will be the same as if both carriers were mobile, but there may be an initial quasistatic distribution which may persist relatively unchanged for a long time.

In many physical cases, it will be a poor approximation to assume that the charge carriers can approach arbitrarily close to the blocking electrode. Thus, in electrolytes, the center of a charged ion will certainly be unable to approach much closer than the normal ionic radius. If there is negligible ionic chemisorption at the polarized electrode, the double layer may be characterized by an essentially surface charge on the electrode, a region next to the electrode containing no charge, and a diffuse-layer region extending into the solution within which the concentration of ions of one sign decreases toward the bulk value and that of opposite polarity increases toward this value. In

some cases, the charge-free layer may consist of a layer of hydration between the electrode and the nearest ions in addition to a layer of thickness determined by the distance of closest approach of the unhydrated ions. The mathematical solutions discussed in this paper apply only to the final diffuse layer in electrolytes. All the above results may be applied for this region, however, provided that it is recognized that the potential across the diffuse layer is not V_0, the total applied potential, but is less than V_0 because of a potential drop in the charge-free layer, and provided that the distance x in the foregoing formulas is measured not from the electrode but from the boundary between the charge-free and the diffuse layers. The present solution is, therefore, not a complete solution for double-layer structure and behavior in electrolytes, but it will be applicable when the charge carriers are electrons. A theory of the complete double layer in unadsorbed electrolytes will be presented in a later paper.

Infrared Reflection Spectra of Phosphate and Arsenate Crystals*

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(Received October 22, 1953)

Crystals of KH_2PO_4, $NH_4H_2PO_4$, KH_2AsO_4, and $NH_4H_2AsO_4$ were examined in the 1–25 micron region. Data were obtained at room temperature for all four crystals, and in addition the spectra of the potassium compounds were examined below their Curie points. In order to avoid the use of thin crystal cuts required for absorption measurements, an optical system was designed which permitted recording of reflection spectra. At the low temperature an increase in the number of bands was observed, and the phosphate and arsenate spectra seemed displaced to higher frequencies. The transition from hydrogen bonding prevailing at room temperature to hydroxyl bonding below the Curie points is considered likely.

I. INTRODUCTION

IN a previous communication to this journal[1] we reported on the infrared reflection spectra of KH_2PO_4, $NH_4H_2PO_4$, KH_2AsO_4, and $NH_4H_2AsO_4$ crystals. These observations have now been extended toward both longer and shorter wavelengths. It is well known that these piezoelectric crystals become ferroelectric below certain temperatures known as the Curie points. These temperatures are 122.0°K, 147.9°K, 95.6°K, and 216.1°K for KH_2PO_4, $NH_4H_2PO_4$,

KH_2AsO_4, and $NH_4H_2AsO_4$, respectively.[2] By far the largest polarization is exhibited along the z axis. We conducted experiments at room temperature and at the temperature of liquid nitrogen, 72.6°K, which lies below the Curie points of these compounds.

When cooled below the respective Curie points, these crystals break up into smaller regions.[2] The potassium salts develop some parallel cracks but generally remain optically homogeneous and transparent. In contrast, $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ shatter completely, becoming an inhomogeneous, nontransparent, white mass.[2,3] For this reason we could make low-temperature measurements with only the potassium salts.

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