

# Space charge in silver halides—Theory of surface charge and electrode charge

J. Ross Macdonald

*Texas Instruments Incorporated, Dallas, Texas 75222*  
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It is suggested that the recent space-charge theory of Fatuzzo and Coppo omits consideration of several effects important in general space-charge situations and probably also important in these authors' experimental studies of silver halides. These effects are discussed in some depth and may explain, at least in part, why Fatuzzo and Coppo's theoretical analysis does not apply well to their experimental results. A detailed discussion is given of the diffusion potential and of surface and electrode charge in blocking and nonblocking electrode situations. Although a careful distinction between electrode and surface (adsorbed) charge is usually made in the ideally polarized electrode (completely blocking) electrolyte case, the need for this necessary separation has apparently not been well recognized heretofore for situations where a solid material of interest is assumed to be contained between electrodes which are completely blocking for some or all types of mobile charge carriers in the solid. When this distinction is made for the problem considered by Fatuzzo and Coppo, quite different results than theirs are obtained. Three important improvements over the Fatuzzo-Coppo work are the present use of more appropriate general expressions for static and differential dielectric constants (or capacitances), the avoidance of their implicit assumption that surface charge is independent of total applied potential difference, and the avoidance of their assumption that the applied potential difference divides equally between the left and right crystal-electrode regions. The new analysis, appropriate for intrinsic materials with completely blocking electrodes, leads to expressions for the differential capacitance of such a system for a specific situation where surface charge may depend on the applied potential difference.

## I. INTRODUCTION

The two recent papers by Fatuzzo and Coppo (abbreviated FC hereafter) on theoretical<sup>1</sup> and experimental<sup>2</sup> effects of space-charge layers in silver halide single crystals aid considerably in elucidating space-charge effects in these materials. There seem to be several points in these papers, however, which need further comment, reinterpretation, and correction.

FC begin by recapitulating the equilibrium space-charge calculations of Kliewer and Koehler<sup>3</sup> and Kliewer<sup>4</sup> where a difference in free energy of formation of positive-ion vacancies and positive-ion interstitials leads, for an isolated neutral crystal, to a surface layer of interstitials and a distributed space-charge layer, having a compensating excess of negatively charged vacancies, extending from the surface into the crystal. But FC's actual situation is somewhat different. They consider a slablike crystal having electrodes in intimate contact with parallel faces. Although they find experimentally quite different results when the electrode material is changed, their free-energy calculations seem to ignore the chemical potential contribution arising from the transition from crystal material to electrode material.

The situation is, however, complicated by FC's theoretical assumption of electrodes which are completely blocking for the mobile charge carriers<sup>1</sup> and their subsequent application of their theoretical results to an experimental situation where the electrodes are only partly blocking.<sup>2</sup> Their theory is therefore likely to be at least somewhat inapplicable to their experiment, and as we shall see, it fails to agree with several of their results.

When the electrodes are completely blocking, it is sometimes reasonable to assume that, in the absence of an externally applied potential, the electrodes will have little effect on the Kliewer-Koehler (abbreviated KK

hereafter) equilibrium double layer. On the other hand, when the electrodes are only partly blocking, their presence will certainly alter this double layer and may even change its polarity. In particular, in the latter case, FC's reference potential  $\phi'_\infty$ , which depends in their theory only on the difference in formation energies, may be expected to be considerably different from that pertinent when the crystal is surrounded only by air. No theory of how  $\phi'_\infty$  should depend on electrode material was presented by FC, but, in their experimental work,<sup>2</sup> they do propose that aqueous electrodes will alter the intrinsic double layer compared to metal electrodes. No discussion of whether the aqueous electrodes are fully or partly blocking is given, however.

FC begin their calculations by assuming that their crystal is always in thermal equilibrium.<sup>1</sup> Such equilibrium is indeed possible for completely blocking electrodes and static conditions, but it does not apply for FC's actual, incompletely blocking electrodes, dynamic experiments.<sup>2</sup> For incomplete blocking, the application of a step-function potential difference (PD), for example, leads to a unidirectional conduction current which never dies out. A complete analysis of such a situation might well proceed from a minimization of entropy production, as in nonequilibrium thermodynamics. The absence of thermal equilibrium in FC's experiments results in the inapplicability in principle of the KK results, derived for equilibrium conditions only. FC use these results, however, without considering the approximation thereby introduced. Further clarification of the FC approach requires discussion of diffusion potentials and surface and electrode change.

## II. DIFFUSION POTENTIALS AND INTRINSIC SPACE-CHARGE LAYERS

Under most conditions, all homogeneous over-all neutral materials containing mobile charges exhibit in isolation a non-zero dipole made up of a localized

charge on the surface and a distributed net space charge of opposite sign extending on into the interior of the material. For convenience, let us consider the usual situation where the distributed space charge beginning at one surface does not overlap to an important degree that extending inward from the opposite surface.<sup>1-4</sup> There are then many Debye lengths contained in the separation distance between the electrodes. For most present purposes, each electrode-interface region may then be considered separately.

Surface charge can arise from many different sources, depending on the materials and experimental situation being investigated. The Frenkel-KK formation-energy-difference mechanism for ionic crystals has already been mentioned. In the semiconductor field, where electrodes are rarely well approximated as completely blocking, a metal-semiconductor interface will generally involve a diffusion or contact potential,  $V_D$ , and corresponding double layer.<sup>5,6</sup> Even in the absence of electrodes, charged surface states may be unequally populated in the semiconductor case, again leading to an intrinsic double layer which may be described by a  $V_D \neq 0$ . Kliewer and Koehler's calculation for ionic crystals<sup>3,4</sup> seems, in fact, to be something of an analogue for such materials to Bardeen's<sup>7,8</sup> earlier treatment of semiconductor surface-state effects. In addition, the seemingly widely different, completely blocking electrolyte case with specific ionic absorption is similar in involving a surface (adsorbed) excess of ions of the same sign and a diffuse region of distributed space charge extending on into the solution from the outer Helmholtz plane.<sup>6,9,10</sup>

Let us consider a material containing mobile charges of both signs, with arbitrary charge mobilities, and fitted with two plane-parallel electrodes. For completely blocking electrodes, no transfer of charge between the surfaces of the material and the adjacent electrodes is possible. Such an idealization requires infinitely high and thick potential barriers at the interfaces; complete blocking can frequently be well approximated over a limited applied potential difference range by a thin layer of air or wide-band-gap oxide, such as quartz. On the other hand, when the electrodes are only partly blocking, charges of one or both signs can pass any potential barrier present at the interface. In the electrolyte case, a faradaic current can then flow; for complete blocking, when it cannot, the electrodes are defined as ideally polarized.

It will now be convenient to use  $V_D$  as the general diffusion potential and define  $V_{D0}$  as that applying when either there are no electrodes or those present are completely blocking.  $V_D$  and  $V_{D0}$  are defined as the potential of the surface (with zero applied bias) with respect to a zero reference potential in the neutral bulk of the material and are both independent of applied PD. Let the net charge per unit area on the electrode be denoted by  $q_m$ , that on the adjacent surface of the material by  $q_s$ , and the total (integrated) distributed space charge per unit area by  $q_d$ . Charge balance for the electrode and adjacent material requires  $q_m + q_s + q_d = 0$ . When there is no external PD applied to the electrodes,  $q_m = 0$  and  $q_s = -q_d$ . This is the electrolyte point of zero

TABLE I. Some possible conditions of interest.

Case	Final thermal equilibrium?	Elec-trodes present?	Elec-trodes: Completely blocking (B)? Incom-pletely blocking (I)?	External $V_D$ PD applied?	
1	Yes	No	...	...	$V_D = V_{D0} = -\phi_\infty$
2	Yes	Yes	B	No	$V_{D0} \sim -\phi_\infty$
3	Yes	Yes	B	Yes	$V_{D0}$
4	Yes	Yes	I	No	$V_D \neq -\phi_\infty$
5	No	Yes	I	Yes	$V_D$

charge (pzc). When  $q_m = 0$  and  $V_D = 0$  as well,  $q_s = q_d = 0$ . In the semiconductor situation, this is the flat-band condition. When  $q_m = 0$  and  $V_D > 0$ ,  $q_s > 0$  and  $q_d < 0$ .

Now both KK and FC use a non-zero reference potential rather than taking it as zero in the usual way. FC designate this potential by  $\phi'_\infty$  or  $\phi''_\infty$ , depending on whether the crystal considered is intrinsic or extrinsic, respectively. KK use  $\phi_\infty$  for either  $\phi'_\infty$  or  $\phi''_\infty$ . Thus, in the KK situation of case 1 of Table I,  $V_{D0} = -\phi'_\infty = -\phi_\infty$ , where we have omitted primes for simplicity. Although case 1 does not correspond to the FC situation, all other cases shown in Table I do to some degree. One difficulty with the FC approach arises from their failure to distinguish adequately between the several cases, and their consequent application of the KK results outside their defined domain of validity.

Two separate but related effects of the application of an electrode to a material are included in  $V_D$ . First, the presence of an electrode, blocking or not, may change the density of available surface states or sites. Then the actual occupation of the surface sites or states by charged entities will be altered. Second, when the electrode is not completely blocking, the difference in the composition of the electrode and bulk material (work-function difference in the semiconductor case) will have a direct effect on the surface and distributed space charge. Finally,  $V_D$  takes account of all nonelectrode related effects, such as that represented by  $\phi_\infty$  in the KK situation. Thus, the  $V_{D0}$  for case 2 of Table I is not likely to be exactly the same as that for case 1.

FC consider the  $V_{D0} \neq 0$  situation. Since most previous space-charge treatments<sup>11-16</sup> have dealt explicitly only with  $V_{D0} = 0$ , however, it is of interest to discuss that situation first. One needs to distinguish two different  $V_{D0} = 0$  cases. The first is that where the surface concentrations of positive and negative charges are taken identically zero and remain so for all applied PD values of interest. Let  $V_a$  be the applied PD, with the right electrode positive, the left negative. Then the second case is that where nonzero positive and negative surface-charge concentrations are completely balanced (at least on a semimicroscopic scale) at  $V_a = 0$ , so there is no net average surface charge.<sup>6</sup> Clearly, in this second situation,  $V_a \neq 0$  will generally disturb this balance and produce a net surface charge. Thus, even

when  $V_{D0}=0$ , one should not necessarily ignore surface charge, especially for completely blocking electrodes.

When the electrodes are completely blocking, no charged particles can pass the interface between electrodes and material and, for ideal blocking, there is no thermal equilibrium between electrodes and crystal material even though they are at the same temperature. Thus, all current between electrodes and crystal must be displacement current only. But even with complete blocking, surface charge is not generally blocked from passing to and from the bulk of the crystal by means of a true conduction current.

For partially blocking conditions on the other hand, the usual case of interest is that where the electrodes are completely blocking for mobile charges of one sign and completely nonblocking (free discharge with an infinite discharge rate) or partially blocking for charges of opposite sign.<sup>14,17-19</sup> When  $V_D \neq 0$  and there is a surface charge made up predominantly of charges of a single sign, one must then distinguish between the cases where the majority surface charge is or is not completely blocked by the electrode. When it is not completely blocked, and  $V_a \neq 0$ , it may disappear when static conditions are attained. It will not disappear but will lead to a steady current, however, if a non-zero concentration of such charge can be steadily maintained by transport from the bulk or from the electrode. Since the sign of any net surface charge will generally depend on the sign and magnitude of  $V_a$ , the details of the charging/discharging process may be expected to depend appreciably on  $V_a$  when the electrodes are not completely blocking for mobile charges of both signs.

### III. CAPACITANCE CALCULATIONS AND RESULTS

FC are primarily concerned<sup>1</sup> with calculating static, differential, and dynamic dielectric constants of their intrinsic material, completely blocking electrodes,  $\phi'_\infty \neq 0$  situation. Now the dielectric constant of a system is properly an intensive property of the material involved. But neither the capacitance/unit area arising from a space-charge situation nor a "dielectric constant" derived from it in the usual way (multiplication by the electrode separation, an extensive quantity, as FC have done<sup>1,2</sup>) is generally intensive.<sup>17,18</sup> Thus, rather than use an effective dielectric constant and thereby abrogate the proper meaning of the term, one should more appropriately deal with the over-all specific capacitance (and conductance or resistance) of distributed space-charge systems. Therefore, in this section I shall convert FC's "dielectric constant" results to specific capacitance results. All results apply to an intrinsic situation only.

For the present case of many Debye lengths contained between the electrodes, let us use  $l$  and  $r$  subscripts to distinguish quantities evaluated for the left and right space-charge regions. Then  $V_a = V_r - V_l$ , where  $V_r$  is that part of the applied PD between the right electrode and the neutral bulk of the material, and  $V_l$  is that between the left electrode and the neutral bulk.  $V_r$  is positive,  $V_l$  negative.

To calculate the static (or integral) specific capaci-

tance,  $C_s$ , of the two-electrode system, FC use an expression for surface fields which is equivalent to

$$C_s = (q_{dl} - q_{dr})/2V_a. \quad (1)$$

Here  $q_{dr}$  and  $q_{dl}$  are the total integrated, distributed space-charge concentrations per unit area for the right and left sides. Their calculation is discussed in the Appendix. For simplicity, the unit area designation for charges and capacitances will frequently be omitted hereafter. The corresponding surface charges,  $q_{sr}$  and  $q_{sl}$ , are also discussed in the Appendix. For completely blocking electrodes, it is necessary that  $q_{mr} = -q_{ml}$ . In addition, separate neutrality of the right and left regions of the crystal requires that  $q_{mr} = -(q_{sr} + q_{dr})$  and  $q_{ml} = -(q_{sl} + q_{dl})$ .

The FC expression for  $C_s$  may now be rewritten

$$C_s = \left( \frac{q_{mr} - q_{ml}}{2V_a} \right) + \left( \frac{q_{sr} - q_{sl}}{2V_a} \right). \quad (2)$$

This expression is generally incorrect. It only leads to the correct expression,

$$C_s = (q_{mr} - q_{ml})/2V_a, \quad (3)$$

when  $q_{sr} = q_{sl}$ . Now FC have evidently implicitly taken their surface charges (arising from  $\phi'_\infty \neq 0$  only) independent of  $V_a$  and equal. As we shall see, such independence is incorrect in general, and one should start with Eq. (3), not Eq. (1). Next note that Eq. (3) itself is only correct and consistent with the usual results,  $C_s = q_{mr}/V_a = -q_{ml}/V_a$ , provided the completely blocking electrodes relation,  $q_{mr} = -q_{ml}$ , is satisfied. In the Appendix it is shown that when  $V_{D0} \neq 0$ , the relations  $-V_l = V_r = \frac{1}{2}V_a$  used by FC in their calculation of  $C_s$  are incorrect. It thus turns out that their  $q_{mr} \neq -q_{ml}$ , and their calculated  $C_s$  is therefore itself incorrect for a second reason. A full analysis of the present problem requires consideration of the situation where surface charge does depend on  $V_r$  and  $V_l$ , as in the electrolyte specific ionic adsorption case. Such dependence has been included in the treatment presented in the Appendix. Although even the approach outlined there is somewhat specialized, it is particularly appropriate in the present situation for illustrative purposes since no chemical potential parameters beyond  $V_{D0}$  enter it which might have to be determined separately.

The static capacitance of the two electrode-bulk regions in series is most directly calculated from the results of the Appendix through the relations  $C_s^{-1} = C_{sr}^{-1} + C_{sl}^{-1}$ ,  $C_{sr} = q_{mr}/V_r$ , and  $C_{sl} = q_{ml}/V_l$ . Note that this expression for  $C_s$  also only holds provided Eq. (C8) holds and ensures that  $q_{ml} = -q_{mr}$ . Since the differential capacitance,  $C_d$ , is generally of substantially more interest than  $C_s$ , it alone will be considered hereafter.

FC calculated  $C_d$  from the usual relation  $C_d = d(V_a C_s)/dV_a$ , but their result is incorrect in general because of the use of an incorrect  $C_s$  expression. They found

$$C_d = (\epsilon_0/8\pi L_D) \cosh \frac{1}{4} V_a^* \cosh \frac{1}{2} V_{D0}^*, \quad (4)$$

where we have replaced their  $\phi'_\infty$  by  $-V_{D0}$  and  $\epsilon_0$  is the dielectric constant of the bulk material. The superscript asterisk indicates normalization with  $kT/e$  and these quantities have their usual meanings. Equation (4) correctly reduces to  $C_0 \equiv \epsilon_0/8\pi L_D$ , the unbiased capacitance

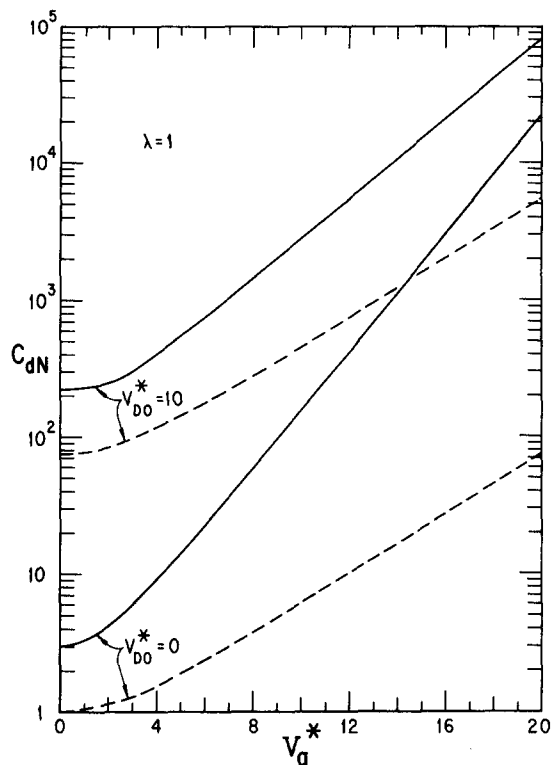


FIG. 1. The normalized differential capacitance  $C_{dN}$  vs normalized applied PD for  $V_{D0}^* = 0$  and 10 and  $\lambda = 1$ . Solid lines: present theory; dashed lines: Fatuzzo and Coppo [Eq. (4)].

per unit area of two ordinary diffuse double layers in series, when  $V_a$  and  $V_{D0}$  are both zero. Here  $L_D$  is the intrinsic Debye length, defined in the Appendix.

Equation (C6) in Appendix C, together with  $C_{dr} = dq_{mr}/dV_r$  and  $C_{di} = dq_{mi}/dV_i$ , leads to

$$C_{dr} = (\epsilon_0/4\pi L_D) \left\{ \cosh\left[\frac{1}{2}(V_{D0}^* + V_r^*)\right] + 2\lambda \cosh\left[\frac{1}{2}(2\lambda V_r^* - V_{D0}^*)\right] \right\}, \quad (5)$$

and

$$C_{di} = (\epsilon_0/4\pi L_D) \left\{ \cosh\left[\frac{1}{2}(V_{D0}^* + V_i^*)\right] + 2\lambda \cosh\left[\frac{1}{2}(2\lambda V_i^* - V_{D0}^*)\right] \right\}, \quad (6)$$

where  $\lambda$  is a parameter introduced in Eq. (B3). It controls the degree to which surface charge is affected by applied PD. When  $\lambda = 0$ , for example,  $V_a$  has no effect on  $q_s$ . By using  $C_d^{-1} = C_{dr}^{-1} + C_{di}^{-1}$  and Eq. (C8) to connect  $V_r^*$  and  $V_i^*$ , one can obtain  $C_d$ . It is clear that the result will be quite different from that of Eq. (4) for any  $\lambda$ , including the plausible  $\lambda \approx 1$  value.

When  $V_{D0} = 0$ ,  $V_r = -V_i = \frac{1}{2}V_a$ , and Eqs. (5) and (6) lead to

$$C_d = (\epsilon_0/8\pi L_D) (\cosh\frac{1}{4}V_a^* + 2\lambda \cosh\frac{1}{2}\lambda V_a^*). \quad (7)$$

When  $\lambda = 0$ , this result is the same as that found many times earlier.<sup>11,16,20,21</sup> It also agrees with FC's result (with  $V_{D0}^* = 0$ ) in this case, but it was FC's primary aim to treat the  $V_{D0}^* \neq 0$  situation. Note that with  $\lambda \sim 1$ ,  $C_d$  will increase much faster with  $V_a^*$  than does the classical expression.

For a single electrode with  $V_{D0}^*$  not necessarily zero,

the above results yield, for  $\lambda = 0$ ,

$$C_d = C_{dr} = (\epsilon_0/4\pi L_D) \cosh\left[\frac{1}{2}(V_{D0}^* + V_a^*)\right], \quad (8)$$

since  $V_r^* = V_a^*$  in this case. This too is a familiar result for situations where surface charge is ignored (inconsistent, however, with  $V_{D0}^* \neq 0$ ), taken independent of  $V_a^*$ , or even taken as a direct part of the electrode charge (incomplete blocking).

Let us now normalize the total differential capacitance  $C_d$  with  $C_0$ . Thus, take  $C_{dN} \equiv C_d/C_0$ . This quantity has been calculated for various  $\lambda$  and  $V_{D0}$  values, and results are shown in Figs. 1 and 2. It should be emphasized that, as discussed in Appendices B and D, the present solution (and that of FC) takes no account of the approach of surface site occupation to its saturated value. Thus, the present  $C_{dN}$  results only apply to those situations where the surface-charge concentration is always much less than its maximum value. In experimental situations,  $C_{dN}$  will not increase indefinitely as  $V_a$  is increased, both because of surface-charge saturation and because of the appearance of new effects, such as breakdown in the high fields near the surface. The limited applicability of the present theory to intrinsic AgCl is discussed in Appendix D.

The solid curves of Fig. 1 were calculated using values of  $V_r^*$  and  $V_i^*$  which satisfy the  $q_{mr} = -q_{mi}$  condition expressed in Eq. (C8). For  $V_{D0}^* = 0$ ,  $V_r^* = -V_i^* = \frac{1}{2}V_a^*$ , but for  $V_{D0}^* > 0$ , one finds that in the  $\lambda = 1$  case the ratio  $R \equiv (-V_i^*/V_r^*)$  starts at unity for  $V_a^* = 0$ , approaches 0.5 as  $V_a^*$  increases, then finally increases again toward unity as  $V_a^*$  further increases. For example, for  $V_{D0}^*$

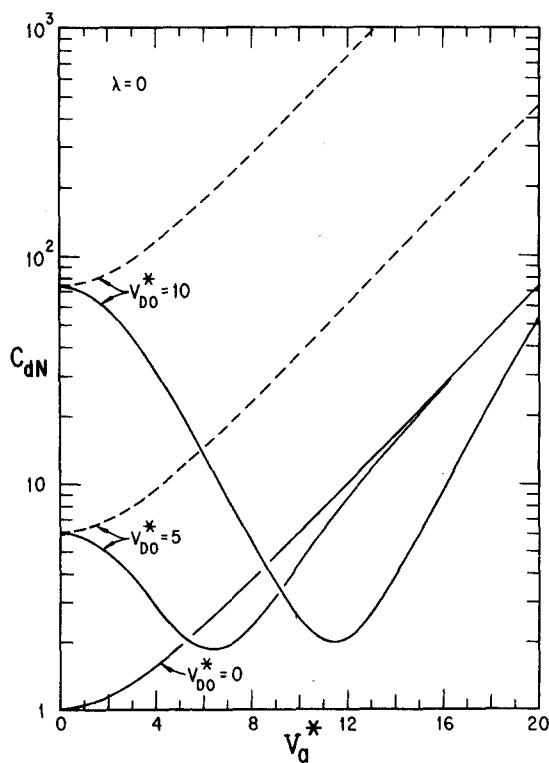


FIG. 2. The normalized differential capacitance  $C_{dN}$  vs normalized applied PD for  $V_{D0}^* = 0, 5$ , and 10, and  $\lambda = 0$ . Solid lines: present theory; dashed lines: Fatuzzo and Coppo [Eq. (4)].

$= 10$ ,  $R$  reaches 0.52 by  $V_a^* = 5$ , achieves a minimum of about 0.50057 near  $V_a^* = 13$ , and has increased to 0.5026 at  $V_a^* = 20$  and to 0.603 at  $V_a^* = 40$ . The larger  $V_{D0}^*$  the closer  $R$  approaches 0.5 and the larger the  $V_a^*$  range over which it remains near this value. Incidentally, note that calculating results for negative values of  $V_{D0}^*$  and  $V_a^*$  is unnecessary. The over-all capacitance is independent of the signs of these quantities; no change in  $R$  occurs when both are negative; and when one is positive and the other negative, the resulting  $R$  is the inverse of that for positive signs.

Figure 1 clearly shows the large difference between the  $C_{dN}$  response for the present  $\lambda = 1$  case and that calculated from FC's result. Note that when  $V_{D0}^* > 0$ , the necessary departure of  $R$  from unity results in a much slower exponential increase of  $C_{dN}$  with  $V_a^*$  than that which would be found with  $R = 1$ . This is illustrated by the slope of the solid-line  $V_{D0}^* = 10$  curve.

Although curves for only  $\lambda = 0$  and 1 are shown, it is worth mentioning that when  $\lambda = 0.5$ ,  $R = 1$  and  $C_{dN}$  reduces to just twice FC's result for all  $V_a^*$ . Figure 2 indicates a great deal of difference between FC's result (whose mode of calculation makes it most appropriate for  $\lambda = 0$ ) and the present  $\lambda = 0$  results when  $V_{D0}^* \neq 0$ . When  $V_{D0}^* = 0$ , they are the same, as shown by Eq. (7).

When  $\lambda = 0$ , Eq. (C8) imposes very different  $R$  vs  $V_a^*$  behavior than that found with  $\lambda = 1$  or 0.5. Again when  $V_{D0}^* = 0$ ,  $R = 1$ . When  $V_{D0}^* > 0$ , however,  $R$  increases continuously from unity as  $V_a^*$  increases until a maximum value,  $R_m \sim V_{D0}^*$ , is reached at  $V_a^* = m$ , then  $R$  decreases slowly toward unity. For example, the following approximate values of  $m$  and  $R_m$  are found:  $V_{D0}^* = 5$ ,  $m \approx 10$ ,  $R_m \approx 4.7$ ;  $V_{D0}^* = 10$ ,  $m \approx 18$ ,  $R_m \approx 10.6$ ; and  $V_{D0}^* = 20$ ,  $m \approx 36$ ,  $R_m \approx 23.8$ . In this latter case,  $R$  still equals 21.7 at  $V_a^* = 40$ . This odd behavior of  $R$  has an interesting concomitant. The quantity  $V_r^*$  approaches  $(V_r^*)_{sat} \approx 1.3863$  at the minimum of  $C_{dN}$  and remains very near this value for an appreciable range on either side of the minimum, with the range increasing as  $V_{D0}^*$  increases. Note that  $\exp[\frac{1}{2}(V_r^*)_{sat}] = 2$ . At the minimum of  $C_{dN}$ ,  $V_a^* = V_{D0}^* + (V_r^*)_{sat}$ , and  $V_i^* = -V_{D0}^*$ . For  $V_{D0}^* = 40$ ,  $V_r^*$  remains in the range  $1.38621 < V_r^* < 1.38632$  for  $20 < V_a^* < 60$ .

Figure 2 shows that because of the fixed surface charge present when  $\lambda = 0$ ,  $C_{dN}$  can decrease appreciably before finally increasing. For large  $V_a^*$ , the final exponentially increasing curve approaches just that for  $V_{D0}^* = 0$ , independent in the limit of the value of  $V_{D0}^*$  itself. Although the solid  $V_{D0}^* = 5$  curve is very close to that for  $V_{D0}^* = 0$  at, say,  $V_a^* = 18$ ,  $R \approx 3.2$  there and  $C_{dr} \neq C_{di}$ . At this point,  $C_{dN} \approx 44.61$ ,  $C_{dr}(\epsilon_0/4\pi L_D)^{-1} \approx 51.47$ , and  $C_{di}(\epsilon_0/4\pi L_D)^{-1} \approx 39.37$ .

Although the present  $C_d$  results for any  $\lambda$  are directly applicable only to an intrinsic situation and to surface-charge concentration much less than the maximum possible, it is hoped that both restrictions will be removed in a subsequent paper.

#### IV. FREQUENCY-RESPONSE COMMENTS

The results discussed in Sec. III also apply when  $V_a$  is sinusoidally time-varying and the applied frequency approaches zero. Here we shall be largely concerned

with results for non-zero frequencies. Further, we shall revert to FC's use of effective dielectric constants rather than specific capacitance. FC denote static and differential space-charge dielectric constants by  $\epsilon_0^*$  and their frequency-dependent dynamic dielectric constant by  $\epsilon^*$ .

We have already considered FC's results for  $\epsilon_0^*$  (converted to specific capacitance) for an intrinsic situation in Sec. III. For the extrinsic case of a crystal containing impurities and measured at sufficiently low temperature (the experimental situation FC actually consider<sup>2</sup>), they only obtain an expression for  $\epsilon_0^*$  at zero bias [their Eq. (31)]. Further, this result appears to predict a value of  $\epsilon_0^*$  much less than even the bulk charge-free ordinary dielectric constant of the crystal,  $\epsilon_0$ , under some possible conditions. Thus, their theoretical results seem not to explain their experimental measurements adequately.

In order to derive their expression for  $\epsilon^*$  for an intrinsic crystal, FC introduce several approximations, some of them possibly rather stringent. In addition, their expression for  $\epsilon^*$  reduces essentially to their  $\epsilon_0^*$  in the limit of zero frequency as it should. But we have seen that their static and differential results are incorrect, both from a failure to calculate and distinguish between surface and electrode charge adequately, and from the use of the incorrect relation  $V_r = -V$ , when  $V_{D0} \neq 0$ . Thus, it is clear that the result for  $\epsilon^*$  must also be in error for several reasons.

FC's expression for  $\epsilon^*$  applies when  $V_a$  contains both an arbitrary-magnitude static and a very small sinusoidally varying component. They suggest that earlier frequency-dependent results of others<sup>13,14</sup> are less appropriate for such a situation than their own result. They correctly point out that this earlier work ignores the effects of any spontaneous or intrinsic space-charge layers (arising from  $V_D \neq 0$ ). But the earlier work explicitly considered only a case-1  $V_{D0} = 0$  flat-band zero-bias situation, one where no static component of the total inner potential (which would include any  $V_D \neq 0$ ) was assumed present. Thus, the two different calculations envisaged different situations and should not be compared on the same basis. It is worth mentioning that a detailed approach to solving some aspects of problems of the present type, blocking or partly blocking, intrinsic or extrinsic, with or without static bias and  $V_D$ , has been presented elsewhere.<sup>19</sup> When the surface-charge considerations of the present paper are combined with the approach of that one, a complete frequency-response solution should be obtainable.

FC's theoretical results for  $\epsilon_0^*$  and  $\epsilon^*$  and their time constant  $\tau$  are highly potential dependent and lead to an essentially exponential increase with applied static potential magnitude. But FC find no such dependence experimentally.<sup>2</sup> Instead, on the application of a PD of 3 V or more, they observe that the measured low-frequency differential capacitance decreases appreciably. They do not attempt to explain this sort of result by detailed comparison with their theory, but it casts doubt on the applicability of the theory to their experimental situation.

The strong theoretical dependence of  $\tau$  on applied PD found by FC indicates that the frequency where  $\epsilon^*$  begins

to approach its low-frequency limiting value should depend strongly on the magnitude of the static PD applied to the crystal during small-signal ac measurements. No such results are described by FC. One possible explanation for the discrepancies between theory and experimental may be associated with FC's suggestion<sup>2</sup> that the surface field arising from the intrinsic space-charge layer is as large as is possible without causing electron or hole injection. Another explanation is that FC obtain theoretical expressions for  $\epsilon_0^*$  and  $\epsilon^*$  when a bias voltage is present only for the pure crystal (intrinsic) case, but they actually measure extrinsic material.

When silver electrodes are employed, FC find<sup>2</sup> that the real part,  $\epsilon'$ , of the measured dielectric constant of a AgCl crystal (presumably at room temperature and presumably unbiased) increases strongly with decreasing frequency below about 100 Hz. On the other hand, they find no corresponding increase above the bulk dielectric constant when a saturated KBr aqueous solution is used for the electrodes. They suggest that the difference arises from a change of the distributed space-charge layer from being made up primarily of negative charges (positive-ion vacancies) to positive charges (interstitial ions) when the electrodes are changed from metallic silver to saturated liquid. It is unfortunate that their theory incorporates no such  $V_D$  effect. A plausible alternate explanation, which may account for some or all of the difference between the two electrode situations, is that the liquid electrodes are considerably less blocking for the mobile charges than are the metallic electrodes employed.

Finally, when metallic electrodes are used, FC's results for the increase in  $\epsilon'$  with decreasing frequency show  $\omega^{-3/2}$  dependence quite closely from about 20 Hz down to about 0.2 Hz, the lowest frequency reached. Since such results cannot be explained by simple single-time-constant Debye dispersion of the type their theory yielded, FC posit the presence of a distribution of relaxation times.<sup>2</sup> A far simpler explanation is available. When mobile charge of one sign is completely or nearly completely blocked and that of the other sign much less blocked and at least partly free to discharge at the electrode, it has been known for some time that  $\omega^{-3/2}$  frequency dependence appears at low frequencies for the measured capacitance of a space-charge situation.<sup>14,17-19</sup> It seems likely that this is the main reason for FC's results with silver electrodes. Possibly interstitial silver ions discharge and are produced (depending on surface field polarity) at the Ag-AgCl surface. On the other hand, the results with liquid electrodes might be explained if the negative charge carriers were appreciably less blocked as well for this situation since no space charge or space-charge capacitance appears when neither positive nor negative charge carriers are blocked.

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#### APPENDIX A: DISTRIBUTED SPACE CHARGE

For the present intrinsic material, the common bulk

concentration of uni-univalent mobile positive and negative charge carriers is  $N_0 = N \exp[-(F^- + F^+)/2kT]$ , where  $F^-$  is the free energy of formation of a cation vacancy and  $F^+$  is simply related to the free energy of formation of a positive-ion interstitial.<sup>1,4</sup> Here  $N$  is the density of anion sites in the crystal and the above expression for  $N_0$  only holds in the usual Boltzmann statistics case of  $N_0/N \ll 1$ .

Now the solution of the single-plane-parallel-electrode space-charge problem for a nondegenerate intrinsic material without recombination has been known since the work of Gouy.<sup>11</sup> It has been repeated many times thereafter (see Ref. 21 for a summary), often, as in the KK and FC cases, without reference to earlier work. Here we do not need the expressions for spatial dependence of the charges and inner potential,<sup>11,12,15,20</sup> but only that for the total net integrated bulk space charge per unit electrode area,  $q_d$ , between the electrode and the neutral bulk of the material. If the inner potential difference between the plane of nearest approach to the electrode of the centers of charge of the diffuse-layer mobile charges and the bulk is denoted  $\psi_b$ , then<sup>11,12,15,20</sup>

$$q_d = -A_1 \sinh\left(\frac{1}{2}\psi_b^*\right), \quad (\text{A1})$$

where

$$A_1 = \left(\frac{2\epsilon_0 k T N_0}{\pi}\right)^{1/2} = \frac{\epsilon_0 k T}{2\pi e L_D} = \frac{4kT}{e} C_0. \quad (\text{A2})$$

Here  $L_D = [\epsilon_0 k T / 8\pi e^2 N_0]^{1/2}$  is the Debye length associated with  $N_0$ . In the present two-electrode case,  $\psi_b = V_r + V_{D0}$  and  $V_l + V_{D0}$  for the right-hand and left-hand sides, respectively. Thus,

$$q_{dr} = -A_1 \sinh\left(\frac{1}{2}(V_{D0}^* + V_r^*)\right), \quad (\text{A3})$$

and

$$q_{dl} = -A_1 \sinh\left(\frac{1}{2}(V_{D0}^* + V_l^*)\right). \quad (\text{A4})$$

Although FC did not calculate  $q_{dr}$  and  $q_{dl}$  explicitly, expressions for them obtained directly from their surface fields are identical to those above except that  $V_{D0} = -\phi'_\infty$ ,  $V_r = V$ , and  $V_l = -V$ , where their applied PD is  $V_a = 2V$ . As we shall see, these values for  $V_r$  and  $V_l$  are incorrect except for the  $V_{D0} = 0$  case. Further,  $V_{D0}$  is not necessarily equal to the KK  $\phi'_\infty = (F^- - F^+)/2e$  when electrodes are present.

#### APPENDIX B: SURFACE CHARGES

The net charge per unit area on the surface of the material,  $q_s$ , will be treated here in analogy to the situation of specific ionic adsorption in the electrolyte case. Then the positive and negative components of  $q_s$  may be related to the corresponding electrochemical free energies of adsorption through adsorption isotherms.<sup>22,23</sup> For concreteness let us initially use the Langmuir isotherm, appropriate for a fixed number of surface sites for positive charges and a fixed number for negative charges. Then,

$$(q_s^+/q_{sm}^+)[1 - (q_s^+/q_{sm}^+)]^{-1} = x_s \exp(-\Delta\bar{G}_s^+/kT), \quad (\text{B1})$$

where  $q_{sm}^+$  is the maximum surface concentration of positive or negative charges;  $\Delta\bar{G}_s^+$  is the standard electrochemical free energy of adsorption; and  $x_s$  is the mole fraction of electrolyte in the bulk of the solution

for the electrolyte situation. Here it is thus just  $N_0/N$ . Note that for Frenkel defects in the present silver halide situation,  $q_{sm}^+ = -q_{sm}^-$ .

For simplicity it is now convenient to define  $\Delta G^\pm \equiv \Delta \bar{G}_\pm^0 - kT \ln(x_s)$ . Solution of Eq. (B1) for  $(q_s^+/q_{sm}^+)$  then yields

$$(q_s^+/q_{sm}^+) = [1 + \exp(\Delta G^\pm/kT)]^{-1}, \quad (\text{B2})$$

consistent with the requirement that when  $\Delta G^\pm \rightarrow \infty$ ,  $q_s^\pm \rightarrow 0$ . Now  $\Delta \bar{G}_\pm^0$  is usually separated into a chemical potential part (involving ionic image attraction to the metal electrode in the electrolyte case) and an electrostatic potential part.<sup>22,23</sup> Let us thus write

$$\Delta G^\pm = \Delta G_0^\pm \pm e\lambda^* V_b, \quad (\text{B3})$$

and

$$\Delta G_0^\pm \equiv (g^\pm \mp \frac{1}{2} e V_{D0}). \quad (\text{B4})$$

Now  $g^\pm > 0$ ;  $V_b$  is either  $V_r$  or  $V_i$ ; and the parameters  $\lambda^*$  take account, at least to some degree, of discreteness of charge effects<sup>6,9,10,22,23</sup> and of any difference in the positions of the equilibrium planes of occupation of positive and negative surface charges, assumed to have valences of  $\pm 1$ . The reason for the above form of the potential-independent  $\Delta G_0^\pm$  will be clear shortly. In the specific adsorption electrolyte case, the potential appearing in an adsorption isotherm, such as the present  $\lambda^* V_b$ , is known as a micropotential.<sup>10,22,23</sup> Although  $\lambda^*$  may depend to some extent on  $q_s^+$  and  $q_s^-$ , any such dependence will be neglected herein, and  $\lambda^*$  will frequently be taken equal to the plausible but approximate value of unity.

Now it will be obvious that Eq. (B2) specifies Fermi statistics for the surface charges, a necessary requirement for identical fixed sites which can each contain only a single charge. For the rest of the analysis I shall pass on to conditions where Boltzmann statistics is a good approximation, however, reserving consideration of the approach to saturated surface occupation (degeneracy) for subsequent analysis. When  $\Delta G^\pm \gg kT$  for all conditions, we may write

$$\begin{aligned} q_s^\pm &= q_{sm}^\pm \exp\{[-g^\pm \mp e(\lambda^* V_b - \frac{1}{2} V_{D0})]/kT\} \\ &= q_{so}^\pm \exp[\mp e(\lambda^* V_b - \frac{1}{2} V_{D0})/kT], \end{aligned} \quad (\text{B5})$$

where

$$q_{so}^\pm \equiv q_{sm}^\pm \exp(-g^\pm/kT). \quad (\text{B6})$$

We shall now assume that  $g^\pm$  is independent of  $V_{D0}$  and then show that the result obtained for  $g^\pm$  is entirely consistent with this assumption.

In the "unperturbed" condition where  $V_a = V_b = V_{D0} = 0$ , the effective potential  $V_e \equiv \lambda^* V_b - \frac{1}{2} V_{D0}$  is zero, and  $q_s^\pm = q_{so}^\pm$ . But in this situation there can be no unbalanced surface charge,  $q_s$ . Since

$$q_s \equiv q_s^+ + q_s^-, \quad (\text{B7})$$

it is thus necessary that  $q_{so}^+ = -q_{so}^- \equiv q_{so}$ , or, from Eq. (B6),

$$g^+ - g^- = kT \ln |q_{sm}^+/q_{sm}^-|, \quad (\text{B8})$$

a result clearly independent of  $V_{D0}$  itself. From Eqs. (B5) and (B7), one can write

$$q_s = -2q_{so} \sinh(V_e^*). \quad (\text{B9})$$

Now when  $V_a = V_b = 0$ ,  $q_m = 0$  and  $q_s = -q_d$ . Equations (A3) and (B9) give, for this condition,

$$A_1 \sinh(\frac{1}{2} V_{D0}^*) = 2q_{so} \sinh(\frac{1}{2} V_{D0}^*). \quad (\text{B10})$$

Thus,

$$q_{so} \equiv \pm q_{so}^* = \frac{1}{2} A_1, \quad (\text{B11})$$

and from Eqs. (B6) and (B11),

$$g^\pm = kT \ln |2q_{sm}^\pm/A_1|. \quad (\text{B12})$$

We may now rewrite Eq. (B5) as

$$q_s^\pm = \pm \frac{1}{2} A_1 \exp(\mp V_e^*). \quad (\text{B13})$$

Since the number densities of positive and negative surface charges are given by  $N_s^\pm \equiv \pm q_s^\pm/e$ , Eq. (B13) leads to

$$\begin{aligned} N_s^+ N_s^- &= (A_1/2e)^2 = \epsilon_0 kT N_0 / 2\pi e^2 \\ &= (N\epsilon_0 kT / 2\pi e^2) \exp[-(F^+ + F^-)/2kT]. \end{aligned} \quad (\text{B14})$$

This result is of the usual  $n_0 p_0 = n_i^2$  form appropriate for classical statistics, as it should be. It should now be clear that the form of Eq. (B4) was necessary in order that  $g^\pm$  turn out to be explicitly independent of  $V_{D0}$  in the Boltzmann approximation. It appears that this specific form of  $\Delta G_0^\pm$ , which involves  $\mp \frac{1}{2} e V_{D0}$ , is the only one which allows the neutrality condition to hold for arbitrary  $V_{D0}$  and leads to  $g^\pm$  independent of  $V_{D0}$  when the electrochemical free energy is required to depend linearly on  $V_{D0}$ . The specific assumption that  $\Delta G_0^\pm$  contains a term independent of  $V_{D0}$  as well as one proportional to it may make the surface-charge part of the present theory somewhat specialized, but it does allow one to carry the analysis through without the need for assuming values of any additional parameters, such as specialized numerical values of  $\Delta G_0^+$  and/or  $\Delta G_0^-$ . The results are thus particularly useful in illustrating a situation where the  $q_s^\pm$  depend only on  $V_b$ ,  $V_{D0}$ , and  $A_1$ .

The above analysis shows that in the present situation, where both positive and negative charges are mobile, it is not thermodynamically possible for  $q_s^+$  or  $q_s^-$  to be identically zero when the other of the pair is not also zero for over-all-neutral equilibrium. When  $V_b$  and  $V_{D0}$  are both zero,  $q_s = 0$  but  $q_s^+ = -q_s^- = \frac{1}{2} A_1$ , a definite, required value. When  $q_{sm}^+ = -q_{sm}^-$ , as in the present AgCl situation,  $g^+ = g^- \equiv g_0$ . Not only must  $g_0/kT$  be much greater than unity to satisfy the Boltzmann approximation, but this inequality is also necessary when  $V_b = V_{D0} = 0$  to ensure that  $q_s^+ = -q_s^- \ll q_{sm}^+$ , since the balanced situation  $q_s^+ = -q_s^- = q_{sm}^+$  is not dynamically stable. When  $V_b = 0$  and  $V_{D0}$  is arbitrary, the above expression for  $q_s^\pm$  leads to  $|q_s^+/q_s^-| = \exp(V_{D0}^*)$ . Thus,  $V_{D0}^*$  alone determines this ratio at the PZC, where  $q_m = 0$ .

The present results should also apply in the specific ionic adsorption, ideally polarized electrolyte case (single working electrode) under appropriate conditions. It should be noted, however, that the final expression for  $q_s^\pm$ , above, differs from the sort of isotherm usually used for electrolytes.<sup>22,23</sup> The most significant differences are probably the explicit appearance of the PD-independent  $V_{D0}$  in the present isotherm and the substitution of  $A_1$  here for a preexponential factor usually

taken proportional to the salt or single-ion bulk activity.<sup>23</sup> Since  $A_1$  is proportional to the square root of bulk concentration, the preexponential dependence is thus quite different. Even though  $V_{D0}$  itself will usually depend somewhat on bulk concentration or activity, such dependence cannot change the present isotherm into the usual electrolyte type of isotherm.

It is important to emphasize that the present theory requires that even in the "unperturbed" situation where  $V_a = V_b = V_{D0} = 0$  and  $q_s = q_a = 0$ ,  $q_s^+$  and  $q_s^-$  are not individually zero (for  $A_1 > 0$ ). Thus, to the degree that the present treatment is applicable, previous completely blocking electrodes space-charge treatments in which  $V_{D0} = 0$  and no surface charges are considered are overly idealized, as well as overly specialized by the  $V_{D0} = 0$  assumption.

It will be of interest later to compare  $q_{s0}$  with the average planar concentration of charge of a given sign in the bulk,  $q_{pa}$ . Let the nearest-neighbor distance between lattice ions be  $d$ . Then for cubic crystals like AgCl,  $N \equiv (2d^3)^{-1}$ . Unlike the liquid case where a reasonable approximation to  $q_{pa}$  might be  $eN_0^{2/3}$ , here  $q_{pa} = eN_0d$ . Thus,  $q_{sm} \equiv \pm q_{sm}^* = eNd$  for such a crystal. Note that when  $(q_s^+/q_{sm}^*) \ll 1$ , Eq. (B1) yields, as it should,  $q_s^* \approx \pm x_s q_{sm} = \pm eN_0d \equiv \pm q_{pa}$  when  $\Delta\bar{G}_s^0 = 0$  and  $x_s$  is taken as  $(N_0/N)$ . Finally, let  $V_b = 0$ ; then  $\Delta\bar{G}_s^0 \equiv \Delta\bar{G}_s^0$ , and one finds  $\Delta G_s^0/kT = \ln |2q_{sm}^* x_s / A_1| \mp \frac{1}{2} V_{D0}^* = \ln [(d/2L_D) \times \exp(\mp \frac{1}{2} V_{D0}^*)]$ , a specialized but nevertheless interesting result.

### APPENDIX C: THE BLOCKING-ELECTRODES CONDITION

Because the electrodes are completely blocking, the electrode charge concentrations,  $q_{mr}$  and  $q_{mi}$ , must be zero or equal and opposite. Now

$$q_{mr} = -(q_{sr} + q_{dr}), \quad (C1)$$

and

$$q_{mi} = -(q_{si} + q_{di}). \quad (C2)$$

Thus, it is necessary that

$$q_{di} + q_{dr} = -(q_{si} + q_{sr}), \quad (C3)$$

a basic relation which establishes a connection between  $V_r$  and  $V_i$ .

If we now take  $V_b = V_r$  and  $V_b = V_i$  in Eq. (B9), we obtain

$$q_{sr} = A_1 \sinh(\frac{1}{2} V_{D0}^* - \lambda V_r^*), \quad (C4)$$

and

$$q_{si} = A_1 \sinh(\frac{1}{2} V_{D0}^* - \lambda V_i^*), \quad (C5)$$

where we have set  $\lambda^* \equiv \lambda$  for simplicity. These results are consistent with that obtained by KK in the  $V_a = 0$  case<sup>3</sup> provided  $V_{D0}^* = -\phi_{\infty}^*$ . Note that, depending on the sign of  $V_{D0}$ , they allow  $q_{sr}$  or  $q_{si}$  to change sign as  $V_a$  is increased from zero. The quantity  $q_{mr}$  may now be written

$$q_{mr} = A_1 \{ \sinh[\frac{1}{2}(V_{D0}^* + V_r^*)] + \sinh[\frac{1}{2}(2\lambda V_r^* - V_{D0}^*)] \}$$

$$= 2A_1 \sinh[\frac{1}{4}(1+2\lambda)V_r^*] \cosh[\frac{1}{4}[2V_{D0}^* + (1-2\lambda)V_r^*]], \quad (C6)$$

with  $q_{mi}$  the same except for  $r$  replaced by  $i$ . Now, Eqs. (A3), (A4), (C4), and (C5) used in (C3) yield

$$\begin{aligned} & \sinh[\frac{1}{2}(V_{D0}^* + V_r^*)] + \sinh[\frac{1}{2}(V_{D0}^* + V_i^*)] \\ &= \sinh(\frac{1}{2} V_{D0}^* - \lambda V_r^*) + \sinh(\frac{1}{2} V_{D0}^* - \lambda V_i^*), \end{aligned} \quad (C7)$$

or

$$\begin{aligned} & \sinh[\frac{1}{2}[V_{D0}^* + \frac{1}{2}(V_r + V_i)]] \cosh(\frac{1}{4} V_a^*) \\ &= \sinh[\frac{1}{2}[V_{D0} - \lambda(V_r^* + V_i^*)]] \cosh(\frac{1}{2} \lambda V_a^*), \end{aligned} \quad (C8)$$

where  $V_a^* = V_r^* - V_i^*$  has also been used. Equation (C8) is an implicit expression for  $V_r^* + V_i^*$ , which, together with  $V_a^*$  allows  $V_r^*$  and  $V_i^*$  to be separately obtained.

It is clear from Eq. (C8) that when  $V_{D0} = 0$ ,  $V_r + V_i = 0$  and  $V_r = -V_i = \frac{1}{2} V_a$ , the FC result. But FC incorrectly use this simplification for all  $V_{D0}$ . Even when  $\lambda = 0$ ,  $V_r \neq -V_i$  when  $V_{D0} \neq 0$ . It is also interesting to note that  $V_r + V_i \neq 0$  in even the  $\lambda = 0$ ,  $V_{D0} = 0$  case with recombination, that where neutral centers uniformly distributed in the bulk partly dissociate to yield mobile charges of one sign and fixed charges of the other sign.<sup>24</sup> Then, instead of having charge accumulation regions (of opposite sign) near the two electrodes, one has an accumulation region at one and a depletion region at the other.

### APPENDIX D: INTRINSIC AgCl

FC's experiments<sup>2</sup> are concerned with extrinsic AgCl, presumably at room temperature. Since the present theory and most of that<sup>1</sup> of FC involve an intrinsic situation, however, and such a situation for AgCl is also treated by Kliewer,<sup>4</sup> we shall here investigate the applicability of the present work for intrinsic AgCl.

Let us take AgCl at  $T = 600$  K. Then if the impurity concentration is sufficiently low,<sup>4</sup> the material will be intrinsic. Ignore any change of  $\epsilon_0$  with temperature and take it as<sup>2</sup> 12.8. It follows from the work of Kliewer<sup>4</sup> that  $e\phi_{\infty}^*/kT \approx 7.5$  and  $L_D \approx 2.4 \times 10^{-7}$  cm. Let us consider completely blocking electrodes and somewhat arbitrarily set  $V_{D0} = -\phi_{\infty}^*$ . Then one finds that  $\frac{1}{2} V_{D0}^* \approx 3.75$ . Further calculation yields  $C_0 \approx 2.4 \mu\text{F}/\text{cm}^2$ ,  $A_1 \approx 0.49 \mu\text{C}/\text{cm}^2$ , and  $q_{pa} \approx 0.014 \mu\text{C}/\text{cm}^2$ . For AgCl,  $q_{sm}^+ = -q_{sm}^- \approx 104 \mu\text{C}/\text{cm}^2$ , as calculated from the normal lattice constant without correction for thermal expansion. From Eq. (B12), one then finds that  $g_0/kT \approx 6.04$ .

Equation (B4) and the above results lead to  $\Delta G_0^+/kT \approx 9.8$  and  $\Delta G_0^+/kT \approx 2.3$ . Thus, when  $V_a = 0$  (or  $\lambda = 0$ ), Eq. (B5) yields  $q_s^-/q_{sm}^- \approx 6 \times 10^{-5}$  and  $q_s^+/q_{sm}^+ \approx 0.09$ . The positive surface charge is clearly not very much smaller than its saturated value even when no external PD is applied, and the present theory, based as it is on the Boltzmann approximation to the Fermi distribution, is therefore inapplicable to this particular situation. Only if  $V_{D0}^*$  were appreciably smaller (possibly because of the presence of electrodes) and/or  $g_0$  appreciably larger would it apply adequately. For  $\lambda > 0$ , applicability is more limited than for  $\lambda = 0$  since  $V_r^*$  and  $V_i^*$  will have opposite signs in  $\frac{1}{2} V_{D0}^* - \lambda V_r^*$  and  $\frac{1}{2} V_{D0}^* - \lambda V_i^*$ . A proper solution of the problem for any  $\lambda$  in the region near saturation probably requires minimization of the



total free energy of the system taking all possible surface site occupation arrangements into account.

Finally, it is worth mentioning that were it possible to obtain a AgCl crystal sufficiently pure to be intrinsic to good approximation at 300 K, the present results would apply somewhat even for  $\lambda=1$ . At this temperature,  $L_D \approx 1.8 \times 10^{-4}$  cm;  $\frac{1}{2} V_{D0}^* \approx -e\phi'_0/2kT \approx 6.2$ ;  $C_0 \approx 3.2 \times 10^{-3}$   $\mu\text{F}/\text{cm}^2$ ;  $A_1 \approx 3.3 \times 10^{-4}$   $\mu\text{C}/\text{cm}^2$ ;  $q_{pa} \approx 1.3 \times 10^{-8}$   $\mu\text{C}/\text{cm}^2$ ; and  $g_0/kT \approx 13.4$ . Thus,  $\Delta G_0^-/kT \approx 20$  and  $\Delta G_0^+/kT \approx 7.2$ . It follows for  $V_a=0$  that  $q_s^-/q_{sm}^-$  is negligible and  $q_s^+/q_{sm}^+ \approx 7.5 \times 10^{-4}$ , sufficiently small for the Boltzmann approximation to hold quite well. Although the present treatment thus applies in the  $\lambda=0$  case, it is much more limited for  $\lambda=1$ . Suppose we maintain the Boltzmann approximation up to  $|q_{sr}/q_{sm}^+|$  or  $|q_{sl}/q_{sm}^-| \leq 10^{-2}$ . Then, for the present  $\lambda=1$  case, we find the following possible ranges:  $0 \leq V_r^* < 15$  and  $-2.6 < V_t^* \leq 0$ . If  $-V_t^*/V_r^* \approx 0.5$ ,  $V_a^*$  is then limited to less than 8.

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