

THE INFLUENCE OF SURFACE CONDITIONS AND SPACE CHARGES ON THE CONDUCTIVITY OF POOR CONDUCTORS

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Surface conditions.—To keep a substance non-conducting it is necessary not only that it does not itself generate carriers of electricity, but that these are prevented from entering if good conductors are brought into contact with it. Vacuum and crystals are insulators because the electrons from metal electrodes cannot leave the metal on account of the work function. Water has electrolytic, not electronic conductivity, because ions can be discharged at the electrodes, while electrons cannot permeate the surface directly.

Space charge.—The possible types of space charge in a medium containing ions of constant and equal mobility are discussed. It is pointed out that for the potentials which are of interest diffusion plays a role only in the immediate neighborhood of the electrode, and space charge is entirely due to insufficient recombination. Methods of determining the data of interest from space charge curves are given. The number of ions present is always below the equilibrium number.

1. THE NATURE OF POOR CONDUCTORS

A GOOD conductor is a substance which contains a sufficient number of electric carriers (electrons or ions) having a sufficient mobility. What groups of substances satisfy these conditions will ultimately be answered only by the new quantum theory, but a qualitative answer is well known at present in that electronic conductors are, in the main, metals and a number of salts, while ionic conductors are other salts in the solid state and a number of solutions in which dissociation occurs. The physical conditions under which dissociation occurs have been treated extensively, and shall not be taken up here. But it is not quite sufficient that carriers are generated in the substance, the substance must also be able to keep them. In the case of a metal, this is due to an attraction between the ionic lattice and the electron. The energy of this attraction has recently been estimated by Bethe¹ and found to be of the order of magnitude of 15 volts. (We are going to measure energy in the familiar manner in volts). This energy is sufficient to keep the electrons in the metal in spite of a large internal pressure, which is, according to Sommerfeld,² due to their highly degenerated state. The resultant of the two, the work function, is still of the order of magnitude of about 5 volts, and accordingly is sufficient to make the equilibrium concentration of the electrons outside negligibly small at normal temperatures, as each volt difference decreases the equilibrium concentration by a factor $e^{-Ve/kT} = 10^{-18}$. Therefore, if we put two metal plates opposite each other,

¹ H. Bethe, *Ann. d. Physik* **87**, 55 (1928).

² A. Sommerfeld, *Zeits. f. Physik* **47**, 1, (1928).

the vacuum between them is an insulator because the work function prevents electrons from passing in sufficient number through it. In the same manner a solution of sodium chloride is a conductor because the ions are prevented from evaporating by the heat of hydration which according to Fajans³ is about 70 k-cal., or about 3 volts. It is an interesting problem, which has not yet been solved, to determine why the condition which makes for the generation of carriers makes, at the same time, for a sufficient energy to keep them in the substance.

If now we put a substance which we call an insulator between two metallic plates it is not sufficient that the substance does not contain carriers, but it is necessary in addition that no carriers from the electrodes can pass through. Let us first consider electrons and take as insulator a salt such as sodium chloride. The experiments of Gudden and Pohl⁴ have shown that if electrons are generated by light in the salt they can move freely so that the mobility of electrons would be sufficient.

Next, the conditions at the surface, that is the potential distribution, have to be examined. When the electrons get to the boundary of the crystal plate, they are able to enter the metal without a prohibitive resistance. This means that the potential energy inside the crystal is not less than the potential

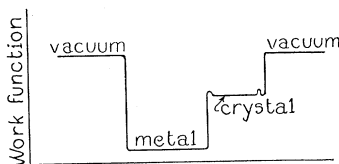


Fig. 1. Work function for different surfaces.

energy (plus internal pressure) of the electrons in the metal. Furthermore, it seems that they cannot enter the metal quite freely,⁵ but only if either a sufficient electron concentration or a sufficiently high field has been reached at the surface of contact. The same seems to be true for the discharge of calcium ions if we electrolyze solid calcium carbonate.⁶ From this it would follow that there is a small hump of energy between the interior of the crystal and the metal. As the results of thermionic emission do not seem to indicate that on the side of the metal there is a hump preventing the free entrance of electrons,⁷ it is probable that this hump lies on the surface of the crystal. The same conclusion can be reached from the fact that the elementary experience shows that it is possible to charge the surface of the crystal without making this crystal conducting. This means that a small hump of potential energy prevents electrons on the surface from penetrating

³ K. Fajans, *f. e., Ber. d. D. Phys. Ges.* **20**, 712 (1918).

⁴ B. Gudden and W. Pohl, many papers in *Zeits. f. Physik.* See B. Gudden, *Hand. d. Physik* **13**, 103, Berlin (1928).

⁵ B. Gudden, *Forsch. d. Ex. Naturwis.* **3**, 150, Berlin (1924).

⁶ A. Joffe, *The Physics of Crystals*, New York, 1928.

⁷ L. Nordheim, *Zeits. f. Physik* **46**, 833 (1927).

into the space of lower potential energy inside. But this hump cannot be very large as moderate fields can overcome it as mentioned before.

The fact that electrons do not pass straight through from one metal into the salt and then out again must, therefore, be due to a high resistance to the entrance of electrons from the metal into the crystal. [It can easily be shown that this entrance is not prevented sufficiently by a space charge which would be set up in the crystal. (See Mathematical Appendix I)]. This means that the potential energy of an electron in the crystal must be considerably higher (its work function lower) than the work function of the metal. Unfortunately there is no way at present to know accurately the amount of work necessary. Joffe⁸ has tried to estimate the work function of the crystal, and found it to be 3.9 volts which then would make the difference about 1 volt.

Coehn⁹ has experimented with contacts between metals and dielectrics. He finds that metals in contact with diamond are always charged positively, which he explains by the assumption that a few electrons enter the diamond. With other dielectrics metals giving off electrons easily are charged positively, nobler metals negatively, which result Coehn explains by an over-compensation of the electron effect through positive ions. It seems quite possible that the very few electrons sufficient to give a measurable charge can be in equilibrium even at room temperature with the metal in presence of a work-function-difference of 1 volt (corresponding to the state at 1500° for 5 volts), but, on the other hand, the apparently rather high potential measured by Coehn makes such an explanation doubtful. Besides, the surfaces with which he experiments are moved against each other.

In a similar manner we can discuss the question why, if we put two metallic electrodes in water and apply to them a potential difference, the current is entirely carried by ions (which fact guarantees the fulfillment of Faraday's law) instead of being carried by electrons which move simply out of the cathode. These would then probably be attached to a water molecule forming a negative ion H_2O^- which would move with the same speed that ions normally have and then be discharged on the anode. The reason that this does not happen must then be that the work (here we always assume the effects of the internal pressure of the electrons in the metal to be already subtracted) for bringing the electrons from the metal into the water is too high. The work function of the metal being about 5 volts, we can divide the amount of energy to be gained by immersion of the electron into the water into two parts: First, the work gained by attaching an electron to a gaseous water molecule (the electron affinity of water vapor: nothing is known about it except that it is very probably positive). Second we gain the heat of hydration by bringing this negative molecule ion into the liquid water. If we assume this

⁸ A. Joffe, *The Physics of Crystals*, p. 142, New York (1928); P. Tartakovsky, *Jour. Russ. Phys. Chem. Soc.* (1926).

⁹ A. Coehn and A. Lotz, *Zeits. f. Physik* 5, 242 (1921); A. Coehn and A. Curs, *Zeits. f. Physik* 29, 186 (1924); A. Coehn, *Fortschr. Ex. Naturwiss.* 1, 174 Berlin (1922).

to be of the same order of magnitude as for Cl^- it will correspond to about 3 volts.

We have then finally to inquire¹⁰ how ions are discharged on the surface of the electrode (we restrict ourselves to ions different from the metal ions of the electrode itself). Assume that we have a positive ion of an electron affinity higher than the metal itself. The following will be a simplified picture of the surface of the cathode: The interior of the metal with a certain potential energy (minus effect of internal pressure); on the surface a rapid rise of potential energy corresponding roughly to the work function; at a distance of about atomic dimensions a layer of positive ions in the liquid in which the potential energy is lower even than in the metal; in the sheet between the surface of the metal and the center of the ions, a strong field

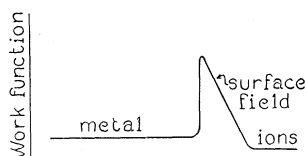


Fig. 2. Work function near an electrode with a layer of positive ions.

simplified as being linear, and of the order of magnitude of the ratio of the electron affinity of ions to atomic dimensions. The new quantum mechanics¹¹ has shown that it is possible for electrons to pass through this rather high energy hump (of about 5 volts) provided that it is sufficiently thin,¹² in other words, that the field is sufficiently high. The ease of transition is very sensitive to the field, just in the range which appears reasonable for the magnitude of this field. It can then easily be understood that the discharge will go smoothly for small ions or for media where the hump is small, while in less fortunate cases it might be possible to raise the field artificially either by an accumulation of ions or by an outside field of sufficient strength.

In the case of negative ions, where the transition occurs from the ion to the electron the qualitative statement is quite similar.

2. SPACE CHARGES IN LIQUID OR SOLID INSULATORS

The general equations for the distribution of charges in an electric field as determined by this field, diffusion and the normal processes of generation and recombination of these ions can easily be stated but their exact integration in the general case has been impossible. According to the circumstances, different assumptions for the purpose of simplification have to be made. Many of them have already been applied to gas discharges and we can simply take over the result. We start with a systematic discussion.

¹⁰ K. F. Herzfeld, to appear shortly in *Zeits. f. Phys. Chem. Abt. B.*

¹¹ R. H. Fowler and L. Nordheim, *Proc. Roy. Soc.* **A119**, 173 (1928).

¹² Physically this comes about as a result of the fact that electrons behave like waves. A wave can pass through a plate to some extent however high its absorption coefficient, provided the plate is thin enough.

A. The velocity of the carriers is mainly determined by the field. This case applies to discharges in highly rarefied gases with long free paths. It has been worked out especially by Child, Langmuir and Schottky,¹³ and gives the familiar results for vacuum tubes, but does not apply to liquids or solids where the friction is large.

B. Due to frictional effects, the main velocity of the ions is the thermal velocity, only slightly modified by the electric field. In this case, as has been shown by Townsend,¹⁴ the ratio between the diffusion coefficient D and the electric mobility K is given by

$$\frac{K}{D} = \frac{e^2\epsilon}{kT} = \frac{F^2\epsilon}{NRT} \quad (1)$$

where e is the charge of an ion, ϵ the dielectric constant, $k = R/N$ the Boltzmann constant (= gas constant R divided by number of molecules per mol N) and e (= the Faraday equivalent F divided by N), the charge of an ion.

For the following we assume that q positive and negative ions are produced per cm^3 per second, which recombine at a rate given by $\alpha n_+ n_-$.

We assume an infinite condenser with parallel plates at a distance 1 from each other, so that everything depends only on the coordinate at right angles to them which we call x , and measure from an origin in the middle between the plates.

In the appendix we have made a study of the space charge distribution which follows from the different approximations which have to be made. The result is the following: Except for a potential drop of the order of magnitude of a few volts the effect of diffusion can be neglected. This can be seen if we consider the relative importance of the current due to diffusion and the current due to the electric field in the equation for the stream of ions passing a certain cross section (V potential, h field):

$$D \left(\frac{dn}{dx} - \frac{F}{RT} nh \right) = Dn \left(\frac{d \ln n}{dx} - \frac{F}{RT} h \right) = Dn \frac{1}{\Delta x} \left[\Delta \ln n + \frac{F}{RT} \Delta V \right] \quad (2)$$

Here the first member is due to diffusion, the second to the electric field. Now even if n should change in the region considered from 10^{20} to 1 ion per cm^3 $\log n$ would change only by 86, which corresponds to a potential of 2.1 volts. This means that if we are interested in space charges corresponding to hundreds of volts we can leave diffusion out of consideration. But, then, the space charge must be due to the fact that the electric current disturbs appreciably the equilibrium between dissociation and recombination of ions. This means further that we can have appreciable space charges only if the current has values which lie in a restricted range near the saturation current. If it were infinitely small compared with the saturation current, the ionization—recombination equilibrium is sustained in the main, except in

¹³ C. D. Child, Phys. Rev. **32**, 492 (1911); I. Langmuir, Phys. Rev. **21**, 419 (1923); W. Schottky, Phys. Zeits. **15**, 526, 624 (1914).

¹⁴ Townsend, Phil. Trans. **193**, 129 (1900).

the immediate neighborhood of the electrodes. If the current is very close to saturation, we have again a constant field, as the ions are then removed so quickly that no space charge can accumulate, as has been shown by Seeliger.¹⁵ We can say that if we want a space charge amounting to the order of magnitude of 100 volts or more, not restricted to a layer very thin compared with the distance between the plates, the current must be between the limits:¹⁶

$$j_{sat}/10 < j < j_{sat}(1 - \gamma/15\beta) \quad (3)$$

The methods of getting from space charge and current measurements, both in the stationary state, and if possible, measurements of the initial current, all the data of interest, namely, number of ions present, mobility, number of ions generated per second, and the recombination coefficient, are discussed in the appendix.

One more point of interest should be mentioned. Joffé has found that after cutting off a field which has acted long enough to build up a considerable space charge, there is an increased conductivity which disappears slowly. The same is true for insulating oils after reversal of the field.¹⁷ Joffé interprets this by assuming that there is an accumulation of ions which is set free after the field is cut off, diffuses back into the main space between the electrodes, and increases there the conductivity until it disappears slowly through recombination. We have shown in the appendix that in the whole region where space charge is considerable, the number of ions is always less than without current. It is possible that there is an excess of ions present, but this must then be due to a resistance to the discharging of ions at the electrode, and they must be concentrated in an extremely thin layer close to the electrode, so thin that the potential drop in it is only a few volts.

APPENDIX I.

SPACE CHARGE DUE TO ELECTRONS BETWEEN PARALLEL PLATES

The point of origin is between the two plates, the distance of which is $2l$. If F is the Faraday equivalent, A and B are constants, then Laue¹⁸ gives the following formula for the electrical density ρ and the potential:

$$\rho = \frac{RT}{F} \frac{2A^2}{\cos^2 Ax} \quad (4)$$

$$V = \frac{RT}{F} \log \cos^2 Ax + B. \quad (5)$$

In the center where the electron density is lowest, ρ is given according to (4) by

$$\rho = 2A^2RT/F.$$

For not too small a distance between the plates the constant A is approximately $\pi/2l$. This gives at room temperature in the center a number of about $NRT\pi^2/2l^2F^2 = 10^6/l^2$ electrons per

¹⁵ R. Seeliger, Ann. d. Physik **33**, 319 (1910).

¹⁶ The first limit meaning space charge limited to about $1/5-1/10$ of the condenser space, the latter a variation in the field of about 10 percent. [(46) and (48')].

¹⁷ Private communication of Professor Whitehead and Dr. Marvin of The Johns Hopkins University.

¹⁸ M. v. Laue, Jahr. der Radio. u. Elekt. **15**, 205, (1918).

cm³ as the number present if it were limited by the space charge and not by the surface forces. This number is high enough to give measureable electron conductivity. Accordingly we conclude from its absence that the surface forces are responsible for the absence of these electrons.

APPENDIX II.

SPACE CHARGE IN AN IONIZED MEDIUM BETWEEN TWO PLATES

We assume a uniform generation of q pairs of ions per second per cm.³ We call the number of positive ions present in 1 cm³ n_+ , the number of negative ions n_- . The recombination per cm³ and second is given by $\alpha n_+ n_-$. We call the diffusion coefficient of the positive ions D_+ for the negative ions D_- , and recall relation (1) between K and D . Let h be the electric field, V the potential, $y = VF/RT$. We assume both ions to have the same charge which might be a multiple of the charge of the electron, in which case F must be taken as a multiple of the Faraday equivalent. ϵ shall be the dielectric constant of the medium. All quantities referring to the left plate ($x = -l$) shall be designated by the subscript 1, all quantities referring to the right plate ($x = +l$) by the subscript 2. The zero point of the potential is taken at the origin in the middle between the plates, the potential difference accordingly $2V_1$. The current density shall be j .

The equations of motion of the ions are

$$D_+ \left(\frac{d^2 n_+}{dx^2} - \frac{F}{RT} \frac{d}{dx} h n_+ \right) = \alpha n_+ n_- - q \tag{6}$$

$$D_- \left(\frac{d^2 n_-}{dx^2} + \frac{F}{RT} \frac{d}{dx} h n_- \right) = \alpha n_+ n_- - q$$

$$\frac{dh}{dx} = \frac{4\pi F}{\epsilon N} (n_+ - n_-) \tag{7}$$

where the last equation is the Poisson equation.

As an exact integration is impossible, approximations have to be made, but can be made in different ways, which shall now be discussed.

1. *Langevin's approximation.*¹⁹ Langevin assumes the number of generated ions to be small, and develops accordingly everything in a power series in q . He shows that this assumption is the more justified the smaller the expression $(ql^2/n_0 D)^2$ becomes, because in this case the loss of ions through diffusion to the plate becomes more and more important compared with recombination. Accordingly he puts

$$\begin{aligned} n_+ &= n_+' q + \dots \\ n_- &= n_-' q + \dots \\ h &= (V_1/l) + h' q + \dots \end{aligned}$$

In our calculations we are going to be satisfied with this approximation. The introduction of these expressions into the equations of motion amount to a neglecting of the recombination term because it would contain q^2 . It is then possible to give a first integral of the following form

$$D_+ \left(\frac{y_1}{l} n_+' - \frac{dn_+'}{dx} \right) = -C_+ + x \tag{8}$$

$$D_- \left(\frac{y_1}{l} n_-' + \frac{dn_-'}{dx} \right) = C_- - x$$

where the left hand sides express the stream of positive or negative ions, respectively (divided by q). The Poisson equation can then be written

$$\frac{dh'}{dx} = \frac{4\pi F}{\epsilon N} (n_+' - n_-') \tag{9}$$

We introduce, then, the following abbreviation

$$\alpha_+ = D_+ y_1^2 / l^2 \quad \alpha_- = D_- y_1^2 / l^2$$

¹⁹ P. Langevin, Le Radium 10, 113 (1913).

and the integration of Eqs. (8) with Langevin's method, but taking into account a generalized surface condition leads to the following formula for the distribution of charges

$$n_+ = (n_+)_2 e^{-y_1} \frac{e^{y_1 x/l} - e^{-y_1}}{1 - e^{-2y_1}} + (n_+)_1 \frac{1 - e^{y_1(x/l-1)}}{1 - e^{-2y_1}} - \frac{2y_1 q e^{-y_1}}{\alpha_+} \frac{e^{y_1 x/l} - e^{y_1}}{1 - e^{-2y_1}} + \frac{y_1 q}{\alpha_+} \left(\frac{x}{l} - 1 \right)$$

$$= \left[(n_+)_{2-} - (n_+)_{1-} - \frac{2y_1 q}{\alpha_+} \right] \frac{e^{-y_1}}{1 - e^{-2y_1}} e^{y_1 x/l} + \frac{y_1 q}{\alpha_+} \frac{x}{l} + \left[(n_+)_{1-} - (n_+)_{2-} e^{-2y_1} + \frac{y_1 q}{\alpha_+} (1 + e^{-2y_1}) \right] \frac{1}{1 - e^{-2y_1}} \quad (10)$$

$$n_- = \left[(n_-)_{1-} - (n_-)_{2-} - \frac{2y_1 q}{\alpha_-} \right] \frac{e^{-y_1}}{1 - e^{-2y_1}} e^{-y_1 x/l} - \frac{y_1 q}{\alpha_-} \frac{x}{l} + \left[(n_-)_{2-} - (n_-)_{1-} e^{-2y_1} + \frac{y_1 q}{\alpha_-} (1 + e^{-2y_1}) \right] \frac{1}{1 - e^{-2y_1}} \quad (10')$$

These introduced into Poisson's equation permit a solution of the latter which gives the following formula for the distribution of the potential

$$V = \frac{V_1 x}{l} + \frac{4\pi F}{\epsilon N} \frac{l^2}{y_1^2} \frac{e^{-y_1}}{1 - e^{-2y_1}} \left\{ \left[(n_+)_{2-} - (n_+)_{1-} - \frac{2y_1 q}{\alpha_+} \right] (1 - e^{y_1 x/l}) \right.$$

$$\left. - \left[(n_-)_{1-} - (n_-)_{2-} - \frac{2y_1 q}{\alpha_-} \right] (1 - e^{-y_1 x/l}) \right\}$$

$$+ \frac{2\pi F}{3\epsilon N} l y_1 q \left(\frac{1}{\alpha_+} + \frac{1}{\alpha_-} \right) \left(\frac{x^2}{l^2} - 1 \right) x + \frac{2\pi F}{\epsilon N} \frac{1}{1 - e^{-2y_1}} \left\{ (n_+)_{1-} - (n_+)_{2-} e^{-2y_1} \right.$$

$$\left. - (n_-)_{2-} + (n_-)_{1-} e^{-2y_1} + y_1 q (1 + e^{-2y_1}) \left(\frac{1}{\alpha_+} - \frac{1}{\alpha_-} \right) \right\} x(x-l)$$

$$+ \frac{4\pi Fl}{\epsilon N y_1^2} \left\{ (n_+)_{2-} - (n_+)_{1-} - \frac{2y_1 q}{\alpha_+} + \left[(n_-)_{1-} - (n_-)_{2-} - \frac{2y_1 q}{\alpha_-} \right] e^{-y_1} \right\} x. \quad (11)$$

Furthermore, we get from (8) as the components of the current carried by the two types of ions separately, if N means again the number of molecules per mol.

$$\frac{F}{N} (-C_+ q + qx) = \frac{FD_+}{N} \frac{y_1}{l} \frac{[(n_+)_{1-} - (n_+)_{2-} e^{-2y_1}]}{1 - e^{-2y_1}} + \frac{F}{N} ql \left(\frac{1 + e^{-2y_1}}{1 - e^{-2y_1}} - \frac{1}{y_1} + \frac{x}{l} \right)$$

$$\frac{F}{N} (C_- q - qx) = \frac{FD_-}{N} \frac{y_1}{l} \frac{[(n_-)_{2-} - (n_-)_{1-} e^{-2y_1}]}{1 - e^{-2y_1}} + \frac{F}{N} ql \left(\frac{1 + e^{-2y_1}}{1 - e^{-2y_1}} - \frac{1}{y_1} - \frac{x}{l} \right). \quad (12)$$

In (11) there is one term, the one multiplied with $x(x-l)$, which is symmetric to the center, while all others are anti-symmetric. This term is due to difference in the behavior of the two ions, either in mobility or at the surfaces.

We assume now first that all ions are discharged immediately upon reaching the electrodes, as in the case of gases. This means

$$(n_+)_{1-} = (n_+)_{2-} = (n_-)_{1-} = (n_-)_{2-} = 0$$

The potential distribution then takes the form

$$V = \frac{V_1 x}{l} - \frac{8\pi F}{\epsilon N} \frac{l^2}{y_1} q \frac{e^{-y_1}}{1 - e^{-2y_1}} \left(\frac{1 - e^{y_1 x/l}}{\alpha_+} - \frac{1 - e^{-y_1 x/l}}{\alpha_-} \right)$$

$$+ \frac{4\pi Fl^2}{6\epsilon N} y_1 q \left(\frac{1}{\alpha_+} + \frac{1}{\alpha_-} \right) \frac{x}{l} \left(\frac{x^2}{l^2} - 1 \right)$$

$$+ \frac{2\pi F}{\epsilon N} y_1 q \frac{1 + e^{-2y_1}}{1 - e^{-2y_1}} x(x-l) \left(\frac{1}{\alpha_+} - \frac{1}{\alpha_-} \right) - \frac{8\pi Fl}{\epsilon N y_1} q \left(\frac{1}{\alpha_+} + \frac{e^{-y_1}}{\alpha_-} \right) x. \quad (11')$$

Again we have the symmetric term with $x(x-l)$ which disappears if the two ions have equal mobility ($\alpha_+ = \alpha_-$), but otherwise is present even without external field.

$$\frac{F}{N} (-C_+ q + qx) = \frac{F}{N} \left(\frac{ql}{1 - e^{-2y_1}} (1 + e^{-2y_1}) - \frac{ql}{y_1} + qx \right)$$

$$\frac{F}{N} (C_- q - qx) = \frac{F}{N} \left(\frac{gl}{1 - e^{-2y_1}} (1 + e^{-2y_1}) - \frac{gl}{y_1} - qx \right)$$

give the components of the current

$$j = 2ql \frac{F}{N} \left(\frac{1 + e^{-2y_1}}{1 - e^{-2y_1}} - \frac{1}{y_1} \right)$$

For very weak fields this gives Ohm's law $j = 2qlFy/3N$ but in the cases with which we are concerned, where y_1 is several hundred, the current is approximately

$$j = 2ql \frac{F}{N} \left(1 - \frac{1}{y_1} \right)$$

or almost saturation current $2qlF/N$, where all the $2ql$ ions generated are discharged at the plates.

Another possible assumption would be that at the positive plate the current is carried entirely by negative ions; at the negative plate, entirely by the positive ions. This means that for $x = -l$ the left hand side of the first equation (8) would be zero; for $x = +l$ the left hand side of the second equation would be zero. This leads to the following connection between the number of ions at the two plates

$$D_+ \frac{y_1}{l} [(n_+)_{1} - (n_+)_{2} e^{-2y_1}] = ql \left[\frac{1}{y_1} - \frac{2e^{-2y_1}}{1 - e^{-2y_1}} \right] (1 - e^{-2y_1})$$

$$D_- \frac{y_1}{l} [(n_-)_{2} - (n_-)_{1} e^{2y_1}] = ql \left[\frac{1}{y_1} - \frac{2e^{-2y_1}}{1 - e^{-2y_1}} \right] (1 - e^{-2y_1})$$

But in this case the current is exactly saturation current since the diffusion is completely overshadowed by the effect of the field.

It might be remarked in general that for the case (11') as well as for the general case (11) (except if the expressions $(n_+)_{2} - (n_+)_{1} - 2y_1q/\alpha_+$, $(n_-)_{1} - (n_-)_{2} - 2y_1q/\alpha_-$ are very small) a large part of the space charge will be restricted to a narrow layer adjoining the plates on account of the very small values $e^{y_1(e^{l-1})}$ takes, except for x very close to l .

As Langevin's approximation gives so nearly saturation current for the voltages with which we are concerned, it does not apply in our case.

2. *Jaffé's approximation.*²⁰ Jaffé gives for relatively small voltages a power development in respect to V_1 , for high voltages a development of inverse powers. But we have to assume with him that the mobilities are equal for both ions.

A) Region of Ohm's low. We put:

$$\begin{aligned} n_+ &= n_+' + n_+'' V_1 + \dots \\ n_- &= n_-' + n_-'' V_1 + \dots \\ h &= h_+' V + \dots \end{aligned} \tag{13}$$

Inserting this into Eq. (6) and (7) we get first equations for n_+' and n_-' , the numbers of the ions that would be present without outside potential

$$D \frac{d^2 n_+'}{dx^2} = \alpha n_+' n_-' - q \tag{14}$$

$$D \frac{d^2 n_-'}{dx^2} = \alpha n_+' n_-' - q$$

$$0 = n_+' - n_-' ; n_+' = n_-' = n'. \tag{15}$$

These values are then determined entirely by diffusion, dissociation and recombination, and it is clear that the number of both kinds of ions should be equal.

$$D \left[\frac{d^2 n_+'}{dx^2} - \frac{F}{RT} \frac{d}{dx} (n_+' h') \right] = \alpha (n_-' n_+' + n_+'' n_+') = \alpha n' (n_+' + n_+'')$$

$$D \left[\frac{d^2 n_-'}{dx^2} + \frac{F}{RT} \frac{d}{dx} (n_-' h') \right] = \alpha (n_-' n_+' + n_+'' n_+') = \alpha n' (n_+' + n_+'') \tag{14'}$$

²⁰ G. Jaffé, Ann. d. Physik **43**, 249 (1914).

are the next approximations for the number of ions with the Poisson-equation:

$$\frac{dh'}{dx} = \frac{4\pi F}{\epsilon N} (n_+''' - n_-''). \quad (15')$$

As we are not interested in the number of ions, we subtract the two equations (14') and integrate once

$$\frac{d}{dx}(n_+''' - n_-'') - \frac{2F}{RT}(n_+'h') = \frac{jN}{DFV_1}.$$

That the letter j , which we have used in the integration constant, is justified follows from the fact that the left hand side multiplied with DV_1 gives the difference of the streams of positive and negative ions. We eliminate then $n_+''' - n_-'''$ with the help of (15'), and find for the field:

$$\frac{d^2}{dx^2}h = \frac{8\pi F^2}{\epsilon NRT}n_+'h + \frac{4j\pi}{\epsilon D}. \quad (15'')$$

In this equation n_+' is to be found from the single equation into which the two equations (14) merge if (15) is taken into account.

$$D \frac{d^2 n_+'}{dx^2} = \alpha n_+'^2 - q. \quad (14'')$$

This equation gives in general upon integration n_+' as an elliptical function of x , as Jaffé has shown, but a numerical evaluation is very inconvenient, and accordingly we pursue another method.

(a) All ions are discharged on the plates as assumed in gas discharges and by Jaffé. We have then the border conditions

$$(n_+)_{1} = (n_+)_{2} = (n_-)_{1} = (n_-)_{2} = 0$$

If we introduce now as abbreviation n_0 the number of ions that would be present without discharge on the plate,

$$\frac{q}{\alpha} = n_0^2, \quad (14''')$$

we get

$$\frac{Dn_0}{q} \frac{d^2(n_+'/n_0)}{dx^2} = \frac{n_+'^2}{n_0^2} - 1. \quad (14'''')$$

We assume now that $(q/Dn_0)^{1/2}x < 1$ (16) and make for n_+'/n_0 a power development according to this expression, stopping with the first member. We find then,

$$\frac{n_+'}{n_0} = \frac{1}{2} \frac{q}{Dn_0} (l^2 - x^2) + \dots \quad (17)$$

This, introduced into (15''), leads to the following differential equation for the field h

$$\begin{aligned} \frac{d^2 h}{dx^2} &= \frac{4\pi F^2 q}{\epsilon RTND} (l^2 - x^2) h + \frac{4\pi j}{\epsilon D} \text{ or} \\ \frac{d^2 h}{d(x/l)^2} &= \frac{4\pi F^2 q}{\epsilon RTND} l^4 \left(1 - \frac{x^2}{l^2}\right) h + \frac{4\pi j N l^2}{\epsilon D}. \end{aligned} \quad (18)$$

We find the following border condition from (15'): $(dh/dx) = 0$ for $x = \pm l$. We then use the abbreviation

$$A = \frac{4\pi F^2}{\epsilon RTN} \frac{q}{D} l^4 = \frac{4\pi F^2 n_0}{\epsilon RTN} \frac{q}{D n_0} l^2 \quad (19)$$

and assume that A is not large compared with 1. Except in the case in which $n_0 l^2/\epsilon$ is larger than 10^4 this is a weaker restriction than (16). We develop the solution in a power series of A stopping with the third and find

$$\begin{aligned} V = \frac{3}{2} \frac{RT}{Fql^2} j x \left\{ C + \frac{A}{6} \frac{x^2}{l^2} \left(C - \frac{2}{3} \right) - \frac{A}{60} \frac{x^4}{l^4} \left(C - \frac{AC}{2} + \frac{A}{3} \right) \right. \\ \left. - \frac{A^2}{360} \frac{x^6}{l^6} \left(C - \frac{AC}{14} - \frac{4}{7} + \frac{A}{21} \right) + \frac{A^2}{6048} \frac{x^8}{l^8} \left(C - \frac{11}{15} AC + \frac{7A}{15} + \frac{A^2 C A^2}{60 \cdot 90} \right) \right\} \quad (20) \end{aligned}$$

where C means the abbreviation

$$C = 1 + \frac{A}{360} \frac{7 - (A^2/16)}{1 + \frac{29}{320}A + \frac{A^2}{960} + \frac{A^3}{3840}} \quad (20')$$

The current j in (20) is then determined by the condition that $V = V_1$ for $x = l$. But formula (20) does not give any stronger space charges with A not large compared with 1 than would Langevin's approximation; in fact, the condition (16) is identical with the latter's condition on page 797, and accordingly (20) is identical, at least in the first order, with (11') for small values of A .

We try next the opposite surface condition, namely that no ions are discharged on the plates under normal conditions without field. Then the number of ions without field is uniformly the equilibrium number throughout space.

$$n_+ = n_- = n_0 = (q/\alpha)^{1/2}.$$

We find then in the same manner which led to (18)

$$\frac{d^2h}{dx^2} = \frac{8\pi F^2}{\epsilon NRT} n_0 h + \frac{4\pi j}{\epsilon D} \quad (21)$$

But this equation is even accurate to a somewhat higher approximation. If we put namely

$$\begin{aligned} n_+ &= n_0 + n''V_1 + n_+''V_1 + \dots \\ n_- &= n_0 - n''V_1 + n_-''V_1 + \dots \end{aligned} \quad (22)$$

the value of $n_+ + n_-$ is not affected by the existence of $n''V$, and so (21) remains unchanged even if we take these members in. The integration of (21) leads then to

$$h = -\frac{jNRT}{2F^2n_0D} A \kappa \operatorname{ch} \kappa x \quad (23)$$

where κ^2 is the constant introduced by Debye²¹ into the theory of strong electrolytes

$$\kappa^2 = \frac{8\pi F^2 n_0}{\epsilon NRT} \quad (23')$$

It appears there for the same reason as here. $1/\kappa$ has the dimensions of a length. A is an integration constant. $\operatorname{sh} x$ and $\operatorname{ch} x$ mean the hyperbolic sin and cosine. Eq. (23) can then be integrated and gives

$$V = -h_0 x + A (\operatorname{sh} \kappa x - \kappa x). \quad (24)$$

There h_0 means the electric field at the origin which is, according to (23)

$$-h_0 = \frac{jNRT}{2F^2n_0D} + A \kappa. \quad (25)$$

If this field were present uniformly between the plates the potential difference would be

$$V_1' = -h_0 l.$$

The constant A is then defined by the excess in potential

$$V_1 - V_1' = A (\operatorname{sh} \kappa l - \kappa l). \quad (26)$$

We can then rewrite (24)

$$V = V_1' \frac{x}{l} + (V_1 - V_1') \frac{\operatorname{sh} \kappa x - \kappa x}{\operatorname{sh} \kappa l - \kappa l}. \quad (27)$$

From (9) and the assumption that the deviations from the uniform distribution are anti-symmetric for both ions ($n_+'' = n_-'' = 0$) it follows

$$n_+ = n_0 + \frac{\epsilon N}{8\pi F} A \kappa^2 \operatorname{ch} \kappa x = n_0 \left[1 + \frac{F}{RT} (V_1 - V_1') \frac{\operatorname{sh} \kappa x}{\operatorname{sh} \kappa l - \kappa l} \right]. \quad (28)$$

²¹ P. Debye u. E. Hückel; Phys. Zeits. **24**, 185, 305 (1923). See also E. Hückel, Erg. der Ex. Nat. **3**, 199 (1924).

But then the condition that (22) should be a convergent series would demand that

$$F(V_1 - V_1')/RT < 1$$

which would again make the space charge potential $V_1 - V_1'$ smaller than a fraction of a volt.

(B) The current is close to saturation. The formulas for this case are completely given by Jaffé. They are

$$h = \frac{V_1}{l} + \frac{2\pi}{\epsilon V_1} q l^3 \frac{RT}{N} \left[2 \left(\frac{1}{D_-} - \frac{1}{D_+} \right) \frac{x}{l} + \left(\frac{1}{D_+} + \frac{1}{D_-} \right) \left(\frac{x^2}{l^2} - \frac{1}{3} \right) \right] \quad (12')$$

$$j = \frac{2qFl}{N} - \frac{RT}{N} \frac{2ql}{V_1} - \alpha \left(\frac{qRT}{N} \right)^2 \frac{1}{D_+ D_-} - \frac{4}{3} \frac{l^3}{V_1^2}$$

3. *Space charge in equilibrium.* Another possible approximation would be given in the case in which we assume that the equilibrium between dissociation and recombination is practically established everywhere, and the action of the electric field is just counter-balanced by diffusion. We neglect then the influence of the current on the space charges. This assumption would be justified if the transfer resistance at the electrodes were very large so that the drain due to the current is small compared with the exchange by diffusion, dissociation and recombination. This case is present in the normal galvanic cells, and has been worked out there.²²

The distribution of ions will then be given by Boltzmann's formula which states the equilibrium between external (for example electric) forces and diffusion, and which does not violate the dissociation—recombination equilibrium.

$$\alpha n_+ n_- = q \quad (29)$$

$$n_+ = n_0 e^{-FV/RT} = n_0 e^{-y} \quad (29')$$

$$n_- = n_0 e^y \quad (29'')$$

The Poisson equation then takes the form

$$\frac{d^2 V}{dx^2} = -\frac{4\pi F}{\epsilon N} n_0 (e^{-y} - e^y) \quad (30)$$

which can be rewritten

$$\frac{d^2 y}{dx^2} = \kappa^2 \operatorname{sh} y. \quad (30')$$

A first integration of this gives, with A as a constant of integration

$$\frac{1}{2} \left(\frac{dy}{dx} \right)^2 = \kappa^2 \operatorname{sh} y + A \kappa^2. \quad (31)$$

This equation can be easily integrated only if A is put $-\frac{1}{2}$. This turns out to represent the case in which the electrodes are infinitely far apart. That shall therefore be assumed and x here calculated from one of the plates, instead of from the middle.²³ We then get

$$\left(\frac{d(y/2)}{dx} \right)^2 = \kappa^2 \operatorname{sh}^2(y/2) \quad \text{or} \quad \frac{d(y/2)}{d(\kappa x)} = -\operatorname{sh}(y/2). \quad (32)$$

We find as a result of integration

$$e^{FV/2RT} = \operatorname{ctgh} \frac{\kappa}{2} (x + x_0) = 1 + \frac{2e^{-\kappa(x+x_0)}}{1 - e^{-\kappa(x+x_0)}} \quad (33)$$

where x_0 is determined by the conditions at the electrode

$$e^{-\kappa x_0} = \frac{1 - e^{-FV_1/RT}}{1 + e^{-FV_1/RT}} \quad (33')$$

²² Gouye, *Comptes rendus* **146**, 612 (1908); *Journ. d. Phys.* **9**, 457 (1910); D. L. Chapman, *Phil. Mag.* **25**, 475 (1913); K. F. Herzfeld, *Phys. Zeits.* **21**, 28, 61 (1920); M. von Laue, and N. Sen, *Ann. d. Physik* **75**, 182 (1924).

²³ For other values of A the solution has to be made by two different developments for y . The calculation is rather lengthy and does not change the conclusions.

or for a considerable value of FV_1/RT

$$\kappa x_0 = 2e^{-FV_1/RT}. \quad (33'')$$

But formula (33) shows that most of the potential drop, apart from a fraction of a volt, is concentrated in a narrow sheet near the electrode. If we call V' the value of the potential at any place where it is higher than 1 volt, we can write for the position of that place

$$\kappa x \sim 2(e^{-FV'/RT} - e^{-FV_1/RT}).$$

From this equation it follows that even if V' is not more than 10 volts κx will be negligibly small, or in other words even with the lowest possible value of κ the whole potential drop, except a few volts, is concentrated in a sheet of very small dimensions.

All the cases considered up to now have shown that whenever diffusion is considered as of preeminent importance while approximations are made in other respects the space charge apart from a few volts is concentrated in the immediate neighborhood of the electrode. In the next case we are accordingly to neglect diffusion completely and will follow a method first outlined by J. J. Thomson.²⁴

4. *Neglection of diffusion.* In this case subtraction of the two Eqs. (6) and integration shows immediately that the electric field is inversely proportional to the sum of the number of ions. If we assume namely that the mobilities of all the ions are equal, the conductivity is proportional to this sum, and the neglecting of diffusion makes the current dependent only on the electric field.

In this case it is shorter to use directly the electric mobility K instead of the diffusion coefficient D . The formula for the current density is then

$$j = eK(n_+ + n_-)h_0 \quad (35)$$

J. J. Thomson then expresses the n 's with the help of this and Poisson's formula through h , and eliminates n from one of the Eqs. (6). The result is

$$\frac{d^2h^2}{dx^2} = \frac{16\pi e}{K\epsilon} \left\{ q - \frac{\alpha}{4e^2K^2h^2} \left[j^2 - \frac{K^2\epsilon^2}{64\pi^2} \left(\frac{dh^2}{dx} \right)^2 \right] \right\} \quad (36)$$

We introduce a new constant

$$\beta^{-1} = \alpha\epsilon/8\pi eK. \quad (37)$$

Langevin²⁵ has shown that β is always larger than 1, and should not vary very much with the material. For air, it is about 4; for quartz, it would come out with Joffe's values about 1. Thomson integrates (36) and finds

$$\frac{K^2\epsilon^2}{64\pi^2} \left(\frac{dh^2}{dx} \right)^2 = j^2 + \frac{qeK\epsilon}{2\pi(1-1/\beta)} h^2 + Ch^{2/\beta} \quad (38)$$

where C is an integration constant. Furthermore, we have for the number of ions the equation

$$n_{\pm} = \frac{1}{2eKh} \left(j \pm \frac{K\epsilon}{8\pi} \frac{dh^2}{dx} \right). \quad (39)$$

If we now neglect diffusion, there can be no negative ions on the positive plate, and no positive ions on the negative plate. It follows then for the plates if we call h_m the maximum value of the field, which is always located at the plate

$$\frac{K\epsilon}{8\pi} \left(\frac{dh^2}{dx} \right)_{h=h_m, x=l} = j$$

With the help of this relation, we can eliminate the integration constant C . We get namely

$$0 = \frac{qeK\epsilon}{2\pi(1-(1/\beta))} h_m^2 + Ch_m^{2/\beta}$$

and find the following differential equation

$$\frac{K^2h_m^4\epsilon^2}{64\pi^2j^2} \left[\frac{d(h^2/h_m^2)}{dx} \right]^2 = 1 + \frac{qeK\epsilon}{2\pi(1-1/\beta)} \frac{h_m^2}{j^2} \left[\frac{h^2}{h_m^2} - \left(\frac{h^2}{h_m^2} \right)^{1/\beta} \right]. \quad (40)$$

This integration has been treated by Thomson²⁴ himself and many others.²⁶ We try a more convenient development in the following manner: we introduce a numerical constant γ , to be defined later, and furthermore the following abbreviations—

$$G^2 = \frac{qeK\epsilon}{4\pi\beta} \frac{h_m^2}{j^2} \quad (41)$$

$$\lambda = \gamma^{1/2} G \frac{8\pi j}{Kh_m^2\epsilon} = \frac{2}{h_m} \left(\frac{4\pi qe\gamma}{K\beta\epsilon} \right)^{1/2} \quad (41')$$

$$u = (h_m^2 - h^2)/h_m^2 \quad 0 \leq u < 1. \quad (41'')$$

With these we rewrite (40) in the following form

$$\frac{\gamma G^2}{\lambda^2} \left(\frac{du}{dx} \right)^2 = 1 + \frac{2\beta G^2}{1-1/\beta} [1-u-(1-u)^{1/\beta}]. \quad (40')$$

We then develop the last expression into a power series up to the second power of u

$$\frac{\gamma G^2}{\lambda^2} \left(\frac{du}{dx} \right)^2 = 1 + 2\beta G^2 (-u + u^2/2\beta) = 1 - G^2\beta^2 + G^2(\beta - u)^2 \quad (40'')$$

But instead of $u - (u^2/2\beta)$ we are going to use $u - \frac{\gamma u^2}{2\beta}$ where γ is a pure number adapted to the value of β , because the table below shows that we get in this manner a better approximation.

u	$(1-u)^{1/\beta} - (1-u)$			$\gamma=1, (u-u^2/2\beta)(1-1/\beta)$			$\gamma=2, (u-u^2/\beta)(1-1/\beta)$		
	$\beta=2$	$\beta=4$	$\beta=10$	$\beta=2$	$\beta=4$	$\beta=10$	$\beta=2$	$\beta=4$	$\beta=10$
0.25	0.116	0.181	0.222	0.117	0.181	0.235	0.109	0.186	0.219
0.50	0.207	0.341	0.431	0.219	0.352	0.475	0.198	0.327	0.427
0.75	0.250	0.457	0.621	0.305	0.510	0.686	0.235	0.457	0.624
0.80	0.247	0.468	0.651	0.320	0.540	0.730	0.240	0.480	0.662

Accordingly one sees that in the range between $\beta=2$ and $\beta=10$ $\gamma=2$ gives a very satisfactory representation up to $u=0.8$, or an h^2 higher than $h_m^2/5$. Accordingly we write, instead of (40'')

$$\frac{\gamma G^2}{\lambda^2} \left(\frac{du}{dx} \right)^2 = 1 + 2\beta G^2 \left(-u + \frac{\gamma u^2}{2\beta} \right) = 1 - \frac{\beta^2 G^2}{\gamma} + \gamma G^2 \left(u - \frac{\beta}{\gamma} \right)^2 \quad (40''')$$

or

$$\frac{\gamma G^2}{G^2\beta^2/\gamma - 1} \left[\frac{d(u - \beta/\gamma)}{\lambda dx} \right]^2 = \frac{\gamma G^2}{G^2\beta^2/\gamma - 1} \left(u - \frac{\beta}{\gamma} \right)^2 - 1. \quad (40''')$$

This equation can be easily integrated. If we take into account that the field must be symmetrical in respect to the center between the plates if the two ions have equal mobility, as is assumed here, we find

$$\frac{h^2}{h_m^2} = 1 - \frac{\beta}{\gamma} + \left(\frac{G^2\beta^2 - \gamma}{\gamma^2 G^2} \right)^{1/2} \text{ch } \lambda x. \quad (42)$$

The square root is determined by the condition that the field h must take the value h_m at the electrodes, $x = \pm l$.

$$\left(\frac{G^2\beta^2 - \gamma}{\gamma^2 G^2} \right)^{1/2} = \frac{\beta}{\gamma} \frac{1}{\text{ch } \lambda l}. \quad (43)$$

²⁴ J. J. Thomson and G. P. Thomson, *Conduction of Electricity through Gases*, Cambridge, 1928, page 193 and the following.

²⁵ P. Langevin, *Comptes rendus* **131**, 177 (1903); O. W. Richardson, *Phil. Mag.* **10**, 242 (1905).

²⁶ G. Mie, *Ann. d. Physik* **13**, 857 (1904); G. W. Walker, *Phil. Mag.* **8**, 650 (1904); A. A. Robb, *Phil. Mag.* **10**, 237, 164 (1905); R. Seeliger, *Ann. d. Physik* **33**, 319 (1910).

The solution of this is

$$\beta G/\gamma^{1/2} = \text{ctgh } \lambda l \tag{44}$$

As the field h_m close to the plates is rather difficult to measure we introduce instead the field h_0 in the middle, which is according to (42)

$$\frac{h_0^2}{h_m^2} = 1 + \frac{\beta}{\gamma} \left(\frac{1}{\text{ch } \gamma l} - 1 \right) \tag{45}$$

We have then

$$h^2 = h_0^2 \frac{1 + \frac{\beta}{\gamma} \left(\frac{\text{ch } \lambda x}{\text{ch } \lambda l} - 1 \right)}{1 + \frac{\beta}{\gamma} \left(\frac{1}{\text{ch } \lambda l} - 1 \right)} \tag{46}$$

If we want now to evaluate a measured field, we try to determine λ by comparing the field h at a given place x with h_0 and calculating λ for an assumed β from the equation

$$\frac{1 - (1 - \gamma/\beta) \text{ch } \lambda l}{\text{ch } \lambda x - \text{ch } \lambda l} = \frac{h_0^2}{h^2 - h_0^2}$$

We can test our assumed β by repeating the process at different places. Knowing then λ , we determine the number of ions n_0 present without field by using (41') and (37)

$$\lambda = \frac{8\pi en_0}{h_0\beta} (2\gamma)^{1/2} \left(1 + \frac{\beta}{\gamma} \left(\frac{1}{\text{ch } \lambda l} - 1 \right) \right)^{1/2} \tag{47}$$

Knowing then n_0 we can get K from the conductivity at very low fields, as we have then Ohm's law $j = h_0 e K 2n_0$. β will then permit the calculation of α and (14''') that of q . The equation for the current is found in (44) and (41)

$$j = \left(\frac{qeK\beta\epsilon}{4\pi\gamma} \right)^{1/2} h_m \text{tgh } \lambda l \tag{48}$$

If λl is sufficiently small we can develop the hyperbolic tangent and find

$$j = qe2l \left(1 - \frac{16\pi qe\gamma}{3K\beta\epsilon h_m^2} + \dots \right) = 2qel \left(1 - \frac{\lambda^2 l^2}{3} + \dots \right) \tag{48'}$$

where $2qel$ is the saturation current.

But we get impossible results, namely a negative value for h_0^2 from (45) if

$$1 + \frac{\beta}{\gamma} \left(\frac{1}{\text{ch } \lambda l} - 1 \right) < 0 \quad \text{or} \quad \text{ch } \lambda l > \frac{\beta}{\beta - \gamma}$$

This is due to the fact that our approximation (40''') gives too small results for the gradient of the field for large values of u , and to get this gradient to be zero at $x=0$, too small a value is assumed for G . As we have mentioned on page 804 we have to limit ourselves to values of u up to 0.8 or

$$\frac{h_m^2 - h_0^2}{h_m^2} < 0.8, \quad \text{ch } \lambda l < \frac{1}{1 - 0.8\gamma/\beta} = 5/3 \text{ for } \beta/\gamma = 2 \text{ or } \lambda l \sim 1, 1$$

or according to (48) $0.73j_{sat} < j < j_{sat}$.

To see what has to be done for lower currents we remember that J. J. Thomson²⁵ in his discussion had divided the region between the electrodes into three parts. In the central part the space charge was negligible, the field constant, adjoining the two condenser plates, there are layers in which the field increases to the value h_m due to the space charges mainly restricted to these layers. For the thickness of these layers and for h_m Thomson gives as approximate formulas

$$l - x_\kappa > \frac{j}{2eq} \quad \text{or} \quad \frac{l - x_\kappa}{l} > \frac{j}{j_{sat}} \tag{49} \qquad \frac{h_m^2}{h_0^2} = \beta^{b/(\beta-1)} = c \tag{49'}$$

At this critical point there is a decided bend in the curve. From (49) one sees that the closer the current is to saturation, the shorter the flat bottom of the curve, that is the region without space charges, becomes. At sufficiently high currents the flat part disappears completely, and the two layers merge in the middle. This is the case for which our preceding discussion applies accordingly.

For the case of weak currents, we have to use Mie's²⁶ approximation. He is forced to use two different expressions for the central part where the space charges are small, and for the parts close to the electrodes where the space charge is large. In his more accurate discussion, the space charge in the center is not completely negligible, and accordingly the curves there are not completely flat. He introduces then a field H defined by

$$H^2 = \frac{j^2}{4e^2 K^2 n_0^2 4l^2} \tag{50}$$

This is the field necessary to uphold the current j if Ohm's law were valid up to the current j with the resistance present at low current. It would also be the initial field if we kept the current constant in time. The general formula is then

$$h^2 = H^2 [1 + 2(c-1)e^{+f}] \tag{51}$$

Here c is a constant defined by (49')

We give a table for c .

β :	1	1.5	2	3	4	6	8	10
c :	$e(=2.72)$	3.38	4	5.20	6.35	8.59	10.77	12.92

f has two different expressions, one in the flat part of the curve, one in the steep part. The two are separated by the point x_k where the bend is located. The values of f are:

Flat part, $x < x_k$ $f = \frac{c-1-(2\beta)^{1/2}}{2(2\beta-c+1)} - (2\beta)^{1/2} \frac{j_{sat}}{j} + \ln \operatorname{ch} \left[(2\beta)^{1/2} \frac{j_{sat}}{j} \frac{x}{l} \right]$ (52)

Steep part $x > x_k$ $f = -\frac{2\beta}{c-1} \frac{j_{sat}}{j} - \frac{\beta(2\beta-c+1)}{(c-1)^2} \frac{j_{sat}}{f^2} \left(1 + \frac{x^2}{l^2} \right) + \ln \operatorname{ch} \left\{ \frac{2\beta}{c-1} \frac{j_{sat}}{j} \left[1 + \frac{2\beta-c+1}{c-1} \frac{j_{sat}}{j} \frac{x}{l} \right] \right\}$ (52')

The position of the dividing point is given by

$$\frac{l-x_k}{l} = \frac{j}{j_{sat}} \frac{(c-1-(2\beta)^{1/2})(c-1)}{(2\beta)^{1/2}(2\beta-c+1)} \tag{53}$$

The value of the coefficient of j_{sat}/j in (53) is shown in the following table:

β :	1	1.5	2	3	4	6	8	10
Coeff.:	1.34	1.08	1.50	1.66	1.79	2.05	2.27	2.45

We remark that (53) differs from Thomson's estimate (49) just by this coefficient.

The evaluation of a given space charge curve will then proceed so: We first decide whether the curve has a flat bottom or a continuous curvature. In the latter case, formula (46) will apply, the current is above $\frac{3}{4}$ of the saturation current. The method of discussion mentioned in connection with (46), (47) will allow the determination of β and λ , (48) will then give the saturation current and from this we get q . In the former case we locate the position of the bend, and then with an estimated value of β , the degree of saturation j/j_{sat} can be calculated from (53). Then we test the two values by comparing more closely the fit of the curve to (52), (52'). A method of trial and error will then lead to the actual values of β and the degree of saturation. Knowing the degree of saturation and the actual current, we can calculate the saturation current, and accordingly q . $q\beta = 8\pi n_0^2 eK$ and either H from (51) or a direct measurement of the initial conductivity which give $n_0 eK$ will allow the calculation of n_0 , the number of ions present without current, and K the mobility separately.

To give an example we investigate the middle curve²⁷ for quartz in Joffe's book, page 103. The data given are scarce so that only a very rough calculation is feasible. We assume the curve

²⁷ Treating it as stationary.

to be symmetric (which seems not to be quite true). Then h_0 is found to be $44/2l$ volts/cm. At the place marked by a circle, which is given by $x=0.8l$, the field on the left side is found to be $124/2l$ volts/cm, on the right $140/2l$ volts/cm. We take as average $132/2l$ volts/cm, or $h^2=9h_0^2$ for $x=0.8l$. We take the bend at $x=0.5l$, and evaluate the formulas for $\beta=1.5, 4, 8$. The corresponding degree of saturation would be $j/j_{sat}=0.45, 0.3, 0.22$. For the ratio h_0^2/H^2 we get from (54) 1.12, 1.003, and 1.0002. This means that for this value of β the reduction of the number of ions in the center compared with the equilibrium number would be 6 percent, 0.15 percent, 0.01 percent. For the field at $x=0.8l$, we find $h^2=1.75h_0^2, 4.59h_0^2, 50h_0^2$. Accordingly the suitable value of β lies around 6, the degree of saturation around 0.26. If the current under these conditions were given we could then calculate j_{sat} and q and proceed as mentioned above.

We show finally that the number of ions present under these conditions is no where larger than the equilibrium number n_0 . According to (35) the ratio h/j is inversely proportional to the number of ions (positive plus negative) present at the place. Formula (50) if applied to the center of the field

$$h_0^2 = H^2 \left\{ 1 + 2(c-1) \exp \left[\frac{c-1-(2\beta)^{1/2}}{2(2\beta-c+1)} - (2\beta)^{1/2} \frac{j_{sat}}{j} \right] \right\} \tag{54}$$

shows that even there h_0 is never smaller than H , and accordingly the number of ions never greater than n_0 . As the field has its lowest value in the center, the same is true for the number of ions anywhere in even greater measure. To prove that this statement holds also when we make the transition to currents close to the saturation current, we proceed in the following manner: If we call h_a the average value of the field taken over the condenser, that is, the total potential difference divided by $2l$, we know that with increasing saturation the ratio of h/j continuously increases. This means that the ratio h_a/H continuously increases. In any case the minimum field is in the center, but we can now write

$$\frac{h_0}{H} = \frac{h_0}{h_a} \frac{h_a}{H}$$

In the preceding analysis, we have seen that close to the saturation current, the variation in the field is less than for low currents (49'), and accordingly for strong currents h_0/h_a is larger than for moderate currents.²⁸ The same is true, as we have just shown, for the second factor h_a/H . We have then proved that the left hand side is always larger than 1 or even the minimum field always larger than the field corresponding to Ohm's law, and therefore the total number of ions present always smaller than the equilibrium number.

²⁸ This argument is not quite strict.