

# THE WIEN EFFECT: DEVIATIONS OF ELECTROLYTIC SOLUTIONS FROM OHM'S LAW UNDER HIGH FIELD STRENGTHS<sup>1</sup>

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## I. INTRODUCTION

Up to sixteen years ago properties of electrolytic solutions were studied by means of conductance data obtained under low potentials and audio

<sup>1</sup> The symbols used in this article are defined as follows:

$\lambda_{E=0}$  = ordinary specific conductance at exceedingly low fields,

$\lambda$  = specific conductance at any field,

$\Lambda_{E=0} \equiv \Lambda_c$  = ordinary equivalent conductance at exceedingly low fields at a concentration  $c$ ,

$\Lambda$  = equivalent conductance at any field,

$\Lambda_\infty$  = equivalent conductance for an infinitely dilute solution at exceedingly low fields,

$\Lambda_{E=\infty}$  = limiting equivalent conductance extrapolated for infinite field,

$E$  = electrical field in E.S.U.,

$E'$  = electrical field in volts per centimeter,

$X$  =  $x$ -component of the field in E.S.U.,

$\bar{V}$  = average potential of the oscillating discharge,

$V_F$  = discharge potential of the spark gap,

$R_{E=0}$  = resistance in ohms at exceedingly low fields,

$R$  = resistance in ohms at any field,

$C$  = capacity,

$L$  = inductance,

$D$  = dielectric constant,

$K$  = dissociation equilibrium constant of the ion pairs,

$c'$  = molar concentration, moles of solute per liter of solution,

$c$  = equivalent concentration, equivalent weight of solute per liter of solution,

$m$  = molal concentration, moles of solute per 1000 g. of solvent,

$z_i$  = valence of the  $i$  ion,

$\Theta$  = time of relaxation of the ion atmosphere,

$\theta$  = decrement (angle),

$\varphi$  = angle,

$\kappa$  = characteristic quantity in the Debye-Hückel theory,

$\psi$  = electrical potential around an ion,

$\rho_i = 1/\omega_i$  = frictional resistance of the  $i$  ion,

$\nu$  = frequency,

frequencies. It was never suspected that electrolytes would exhibit interesting and informative properties under other conditions, and it was not until 1927 that Max Wien discovered that the conductivity of an electrolytic solution increases with increasing field strength when very high electrical fields are applied; in other words, that under such extreme conditions Ohm's law is no longer valid.<sup>3</sup>

This capital discovery, which is of primary importance for the further development of the theory of electrolytic solutions, was the final result of an investigation originally undertaken for the purpose of determining the validity of Stokes' law at high ion velocities. Lenard (16) showed on theoretical grounds that the mobility of an ion should decrease slightly at high speeds. The corresponding decrease of conductivity to be expected for the hydrogen ion, according to theory, was of the order of 0.5 per cent in a field of 1 megavolt per centimeter ( $10^6$  volts per centimeter). The velocity of the hydrogen ion in this field is about 30 meters per second, as compared to about 12 cm. per hour in a field of 1 volt per centimeter. The experimental proof of this prediction presented many difficulties, mainly owing to electrolysis and to the tremendous amount of heat developed in the solution during the time that the resistance is measured. The single-spark method of Wien made such measurements possible; with it Wien showed in 1924 that the conductivity of aqueous solutions of sodium chloride, potassium hydrogen sulfate, and sulfuric acid is independent of field strength within an experimental accuracy of 1 per cent for fields up to 0.5 megavolt per centimeter. This result thus furnished qualitative proof of Lenard's prediction. Later Wien and Malsch, in extending Wien's work to a larger variety of salts and solvents, obtained results that indicated that the temperature coefficient of conductance was somehow influenced by the length of the time interval during which the field was applied (19).

These peculiar results led to a more detailed and accurate study of the phenomenon in question. First, Wien and Malsch developed the baretter method as a new tool which enabled them to measure resistance changes with an accuracy of 1 or 2 parts in 10,000 with fields up to 0.5 megavolt per centimeter (see part II A). Using this method, Wien showed in 1927 that *with high fields the conductance of an electrolytic solution always increases*, and that this effect is not, as was previously supposed, due to an

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$\tau$  = impulse duration,

$\omega$  = frequency in  $2\pi$  sec.,

$\eta_0$  = viscosity of the solvent,

$\alpha$  = degree of dissociation (a parameter in Wilson's theory).

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<sup>3</sup> This fact has been known for solid bodies for some time (26).

anomalous temperature coefficient of conductance, but is a general property of electrolytic solutions, dependent upon the concentration and valency of the ions and the specific character of solute and solvent. He was further able to show that for extremely high fields the conductance tends toward a constant limiting value which corresponds nearly, but perhaps not exactly, to that of the equivalent conductivity at infinite dilution as ordinarily measured at low fields. This phenomenon is now known as the first or normal Wien effect (see part II B).

In these earlier investigations only strong electrolytes were studied. When the work was extended to weak electrolytes, another phenomenon appeared, in that the observed effect was many times larger than that for strong electrolytes. A similar effect had already been observed by Gye-mant in 1928 in solvents of very low dielectric constant ( $D \sim 3$ ). Wien suggested that the large increase in conductance in the case of weak electrolytes is due to an increase in the degree of dissociation. This new effect is referred to as the dissociation field effect or, sometimes, as the second Wien effect (see part II C).

Both of these effects were discovered without the aid of theory. Subsequently, the observed results have been accounted for fairly satisfactorily on the basis of the theory of ion interaction (see part III).

Following the first experimental work in 1922, Wien and his coworkers devoted themselves to studying all characteristics of the field effect. As their work progressed, it became more and more apparent that this phenomenon would be helpful in leading to a better understanding of electrolytic solutions. Since publications relating to the Wien effect have emanated from many different laboratories and have, in the main, been reported in physical journals, which are not readily accessible to chemists, and since no review of these publications has hitherto been attempted, it seemed worth while to undertake a complete review of the literature and to summarize the results in this new field. It is hoped that the present review will prove helpful to chemists in arriving at an understanding of the underlying problems, many of which give promise of important applications and extensions. In writing this review we have carefully considered all reported studies relating to the Wien effect and have attempted to make the bibliography as complete as possible.

## II. EXPERIMENTAL RESULTS

### A. *Experimental technique*

The particular experimental method that may best be employed in studying the conductance of electrolytic solutions with high fields is determined by the properties of the solution, such as the specific conductance,

the temperature coefficient of conductance, the density, the heat capacity, and the field strength used. The main difficulty in carrying out these measurements is to avoid excessive heating of the solution (and attendant change in resistance) during the time required for the resistance measurement. Ordinary methods of resistance measurement may sometimes be used for poorly conducting systems and at moderate fields, but generally, for good conductors and at high fields, reliable results are obtained only by means of *impulse methods*, where the high potential acts for a very short period of time. Even then, the influence of the heat effect upon the resistance measurement cannot be completely eliminated. For example, there is still a rise in temperature of  $0.24^{\circ}\text{C}$ . when a field of 100,000 volts per centimeter is applied for only  $10^{-6}$  sec. to a solution with a specific conductance of  $10^{-4}$  mhos (and density and heat capacity of unity). If the temperature coefficient of conductance is 2 per cent per degree, the corresponding resistance change is 0.5 per cent. This example may serve to illustrate the difficulties that had to be overcome in measuring the deviations from Ohm's law.

Resistance measurements during very short time intervals may be carried out in two different ways. First, instantaneous values of the resistance may be recorded by means of a cathode ray oscillograph (Rogowski), and second, the average resistance change may be measured with ordinary integrating instruments (Wien). Whereas the former method is more direct, it cannot compare in accuracy with the second, more tedious, integrating method.

Another difficulty that appears in carrying out these measurements is due to the fact that it is impossible to obtain (with the usual methods) a constant potential for short time intervals (in the order of one-millionth of a second). This, obviously, has to be considered only for the integrating impulse method, where the exact voltage-time function must be known in order that the average resistance may be correlated with an average potential.

In his single-spark method Wien (32) used damped oscillations obtained by discharging a condenser through a resistance and an inductance. Under these conditions the voltage-time function may easily be calculated, provided the electrical constants of the circuit are known.

Figure 1 shows the diagram of the apparatus used by Wien in his original experiments. By opening  $\text{Sw}_3$  in the primary circuit of the induction coil I, the condensers C are charged to a potential which causes a breakdown across the spark gap S. This starts an oscillating discharge in the circuit S-C-L- $\text{R}_1$  (or S-C-L- $\text{R}_2$ ). The inductively coupled thermocouple Th, together with the galvanometer G, measures the time integral of a current which is proportional to the current oscillating in the

main circuit. Most of the energy stored in the condensers  $C$  is dissipated in the resistance, and therefore the current integral is proportional to the total amount of stored energy,

$$U_0 = V_P^2 C/2$$

and inversely proportional to the resistance. Two resistances  $R_1$  and  $R_2$  can thus be compared in two consecutive measurements, when the rest of the circuit remains unchanged. If  $R_1$  and  $R_2$  are pure ohmic resistances, then equal galvanometer deflections indicate equality of  $R_1$  and  $R_2$ .<sup>4</sup> For measurements with electrolytic solutions  $R_1$  represents the conductance cell, containing the solution, and  $R_2$  a comparison resistor, whose value is independent of field strength.

With the single-spark method Wien was able to measure conductivities of electrolytic solutions in fields up to 500,000 volts per centimeter with

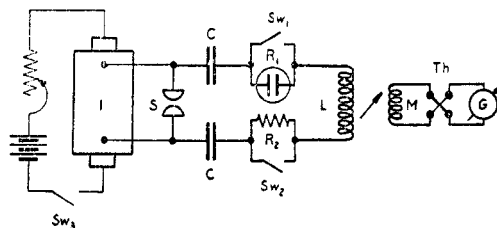


FIG. 1. The single-spark arrangement

an error of about 1 per cent. The accuracy of the method is mainly limited by the relatively poor reproducibility of the spark potential. (Even when radioactive substances are used to ionize the air in the spark gap, it is not possible to eliminate retarded sparks completely.) The field strength of 500 kilovolts per centimeter represents an upper limit determined by the electrical strength of the solution. Moreover, it could only be obtained with special cells (20, 32), for which the calculation of the field strength is very uncertain. In the later quantitative work with ordinary cells, the maximum field strength seldom exceeded 250 kilovolts per centimeter.

In order to enhance precision, a way had to be found that permitted

<sup>4</sup> The same method can be used for measuring complex resistances (see Malsch: *Ann. Physik* **84**, 841 (1927)). In conductance measurements errors may be introduced by neglecting the inherent capacity of the electrolytic resistance. Its influence increases with increasing frequency, increasing dielectric constant of the solution, decreasing cell constant, and decreasing conductivity. See the discussions of Malsch (17), Malsch and Hartley (18), and Michels (21).

comparison of two resistors simultaneously instead of in two consecutive measurements. Malsch and Wien (20) found the solution of this problem in the baretter method. The fundamental circuit is the same as in the single-spark method, figure 1, but the unknown and the comparison resistor are now connected in parallel. The partial currents through these resistors are compared in a baretter bridge, which reduces the determination of high-frequency currents to a resistance measurement with direct current: the high-frequency current heats a thin wire, thus changing its resistance.

Figure 2 shows a typical baretter arrangement. The main circuit is formed by the spark gap  $S$ , inductor  $L$ , condenser  $C$ , and two parallel arms containing  $R_1$  and  $R_2$ . Each one of these arms is coupled to a baretter  $B$  through the resistive coupling unit  $R_k C_k$ .<sup>5</sup> The resistance change of the baretters is measured in the Wheatstone d.c. bridge  $B-B-R_h$ , which is separated from the main high-frequency circuit by choke coils  $Ch$ .<sup>6</sup>

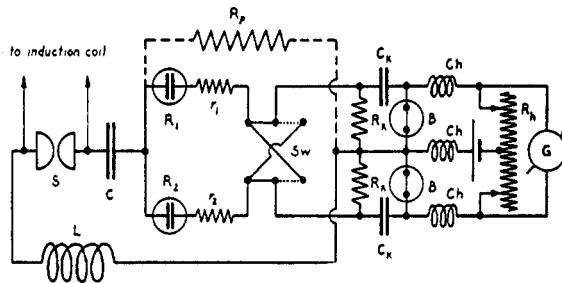


FIG. 2. A typical baretter arrangement

If the resistors in the two arms are equal when the condenser  $C$  is discharged, equal currents flow through the two baretters, thus yielding equal changes of resistance, and the d.c. bridge therefore remains balanced. This method is, consequently, a "null" method.

As baretters, Malsch and Wien used ordinary incandescent lamps,<sup>7</sup> which were selected for having equal resistance as well as equal temperature coefficients. By means of  $R_h$  the direct current in the bridge is adjusted to a point where the resistance changes linearly with increasing

<sup>5</sup> Inductive or capacitive coupling may also be used, but the resistive coupling shown in the diagram has the advantage that one can change the sensitivity over a wide range without largely affecting the electrical constants of the circuit (1).

<sup>6</sup> Schiele (31) eliminated these chokes by constructing baretters which in themselves constitute small Wheatstone bridges.

<sup>7</sup> If Wollaston wires of only a few microns in diameter are used in the baretters, the sensitivity can be increased nearly a hundredfold (31).

current, thus allowing linear interpolations between the galvanometer readings. An alternating switch Sw is used to balance out any remaining irregularities.

Types and arrangements of the resistances in both arms are determined by the special problem involved. The combination shown in figure 2 permits the comparison of two electrolytic resistors. The small high-frequency resistors  $r_1$  and  $r_2$  (33) serve to balance the partial currents. If the inherent cell capacity cannot be neglected (see footnote 4),  $r_1$  and  $r_2$  have to be connected parallel to  $R_1$  and  $R_2$  rather than in series, because otherwise large errors may be introduced (18).

The advantage of this baretter method is that the measurements are independent of irregularities of the spark, so that the much higher sensitivity may be fully utilized. An accuracy of 1 to 2 parts in 10,000 as

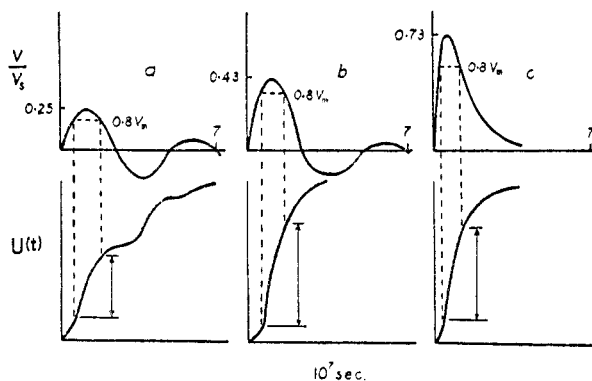


FIG. 3.  $V/V_s$  is the ratio of the instantaneous voltage drop across the resistor to the spark potential.  $\theta = \pi R \sqrt{C/L}$ . In a,  $\theta = 1.0$ ; in b,  $\theta = 2.14$ ; in c,  $\theta = 6.28$ .

obtained by Schiele (28) probably does not represent the upper limit. Furthermore, this method constitutes a general precision method for measurements with high frequencies and high potentials. It is not confined to resistance measurements alone, but may be used to measure inductances and capacities as well.

For both the single-spark and the baretter method, the form of the voltage-time function is of great importance, because it influences the measured resistance average. The curve should have a flat top, which means that the potential is near its maximum value during a large fraction of the time interval during which the discharge occurs; in other words, most of the energy should be dissipated when the voltage is high. Obviously, this condition has to be fulfilled with any integrating method, and by proper choice of the electrical constants in the oscillating circuit it may be fulfilled. In figure 3, at the top, are shown three typical

voltage-time functions, in which the influence of  $L$ ,  $C$ , and  $R$  on their shape is expressed in terms of the logarithmic decrement

$$\theta = \pi R \sqrt{C/L}$$

The lower curves represent the corresponding current integrals or energy-time functions:

$$U(t) = R \int_0^t i^2(t) dt$$

which, for  $t = \infty$ , are equal to  $U_0 = V_p^2 C/2$ . In the case of curve a, only a small amount of the total energy is being dissipated while the voltage drop across the resistor is greater than 0.8 times the maximum voltage  $V_m$  (indicated in the figure by vertical arrows). From curve b, however, it is seen not only that  $V_m$  increases with increasing decrement, but also that a greater portion of the energy is consumed during the time interval that the voltage is within the desired interval. For still larger decrements  $V_m$  increases further, but the amount of energy dissipated in the desired voltage interval now decreases (curve c). For optimum operating conditions it is thus desirable to work with a decrement approximately equal to  $\pi$ .

The impulse duration  $\tau$  is defined as the time of one half-period of the undamped oscillation of the main circuit.<sup>8</sup> For this case,  $\theta = R = 0$ , and

$$\tau = \pi \sqrt{LC}$$

It is seen from figure 3 that for decrements of the order  $\pi$  most of the energy actually is dissipated in such a time interval. With given values for decrement, impulse duration, and total resistance,<sup>9</sup> the electrical constants that yield the desired voltage-time function are,

$$L = \tau R / \theta \quad \text{and} \quad C = \tau \theta / \pi^2 R$$

The experimentally determined values for the relative conductance change,  $\Delta\lambda/\lambda_{E=0}$ , at different field strengths represent the actual conductance changes due to deviations from Ohm's law superimposed on con-

<sup>8</sup> The impulse deviation so defined is only an approximation, since the frequency of a freely oscillating, damped circuit is slightly lower than without damping. The approximation is sufficient for experimental purposes, where only the order of magnitude is of interest. However, it should be considered by comparing experimental data with theoretical results. In this comparison a Fourier analysis of the impulse will indicate whether a correlation of the experimental result with the fundamental frequency,  $\omega = \pi/\tau$ , is justified or whether the influence of harmonics,  $n\omega$ , has to be taken into account.

<sup>9</sup> In the case of the baretter method the parallel resistance of the two arms has to be considered.



ductance changes due to the heating of the solution during the measurement. In order to separate these two effects, the heat effect must be calculated (20) from the energy,  $U_d$ , dissipated in the electrolytic resistor. Because of energy losses in the spark itself,  $U_d$  is smaller than the total amount of energy stored in the condenser,  $U_0$ ,<sup>10</sup> but a corresponding correction,  $p = U_d/U_0$ , can easily be determined calorimetrically. Then, the relative change in conductance due to Joule's heat is simply given by

$$\Delta\lambda/\lambda = \epsilon\beta p V_r^2 C/4m'c^*A$$

where  $m'$  is the mass of the solution between the electrodes of the cell,  $c^*$  the heat capacity of the solution, and  $A$  the mechanical equivalent of heat. The temperature coefficient  $\beta$  is assumed to be independent of field strength.  $\epsilon$  represents the fraction of energy dissipated in the electrolytic resistor; it is equal to 1/2 in the case of the baretter method, where the energy  $U_d$  is dissipated in two equal resistors.

The heat effect may be decreased by decreasing the impulse duration and the energy dissipated in the electrolytic resistor. The latter may be accomplished by inserting a resistor  $R_p$  (figure 2) in parallel with the resistors to be measured (21). Both methods are limited because the deviations from Ohm's law depend, in some degree, upon impulse duration, and because the introduction of  $R_p$  tends to decrease the sensitivity and influence the decrement of the oscillating circuit. The influence of the heat effect may be eliminated by comparing resistors that have the same temperature coefficient of conductance.

The actual deviations from Ohm's law, as obtained from experiments at high fields after correcting for the heat effect, may be referred to corresponding values of the spark potential  $V_r$ . Thus, intercomparisons are possible for measurements that have been carried out with the same decrement and impulse duration. In order to determine the average field strength, which corresponds to a certain measured average conductance, the average potential drop across the resistor must be calculated. This average potential follows from the solution of the fundamental differential equation for a freely oscillating damped circuit, in which the resistance is now a function (assumed known) of the potential. Malsch and Wien (20) considered a linear dependency of conductance and field strength a sufficiently close approximation. They obtained for the average potential in the case of an oscillating discharge ( $\theta < 2\pi$ )

$$\bar{V} = [4\delta(1 + e^{-\sigma})/\{3(1 + 2\delta^2)(1 - e^{-\sigma})\}]pV_r$$

where  $\delta = \theta/\pi$  and  $\sigma = 3\pi\delta(4 - \delta^2)^{-1/2}$ . Dividing  $\bar{V}$  by the distance between the electrodes in the conductance cell finally yields the average

<sup>10</sup> The losses in the condenser and in the inductance coil are negligible.

field strength. In this computation Malsch and Wien neglect the influence of the stray field around the electrodes. They estimate that uncertainties due to this and the preceding assumption as to the relation between resistance and potential are of the order of several per cent (33).

### B. The first Wien effect

There are two types of experiments that show clearly that the conductance of an electrolytic solution increases with increasing field strength.

The first experiment was carried out by Wien (33, 34) with the baretter method and is based on the following principle: The conductance change due to heat is always the same for any form of the voltage-time function, provided the dissipated energy remains unaltered. If, therefore, a change in the form of the voltage-time curve, with otherwise constant parameters

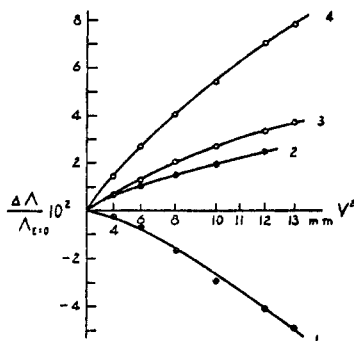


FIG. 4. Acetone solutions of cadmium iodide (curves 1 and 2) and of cobalt chloride (curves 3 and 4), where  $\lambda_{E=0} = 0.002$ . In all four cases  $C = 3029$  cm. In curves 1 and 3  $L = 245,000$  cm., and in curves 2 and 4  $L = 30,000$  cm.

(spark potential and total capacity in the circuit), yields a change of the measured resistance, then this change can only be due to another, superimposed effect which likewise is a function of the field strength.<sup>11</sup> Thus, for a positive field effect, the measured resistance change decreases with decreasing decrement (for  $0 < \theta < \pi$ ; see also figure 3). This actually was observed by Wien (33, 34). Figure 4 shows similar results obtained by Bauer (1) for acetone solutions of cadmium iodide (curves 1 and 2) and cobalt chloride (curves 3 and 4) for two values of the decrement. When this decrement was decreased to 0.34 times the initial value (curves 2 and 4), the effect decreased very markedly (curves 1 and 3). In accord-

<sup>11</sup> The impulse method is applicable only when relatively long impulses are used, under which condition the impulse duration does not influence the magnitude of the field effect, i.e., for  $\tau > 10^{-9}$  sec.

ance with the negative temperature coefficient of conductance of the cadmium iodide solution, the effect even changed its sign.

The experiment by the second method was carried out by Fucks (9) in Rogowski's laboratory, using an instantaneous impulse method. He photographically recorded the voltage drop across an electrolytic resistor with a high-speed cathode ray oscillograph. Figure 5a shows a diagram of the apparatus used. A condenser is discharged into a long line which terminates at the opposite end in the conductance cell  $R_1$  in series with the constant resistor  $R_2$ . The parallel capacity  $C$  balances the effects of the inherent cell capacity and the capacity of the deflection plates in the oscillograph. For a measurement two consecutive exposures with the same potential are made. In the first, the oscillograph is connected across  $BC$ , which gives the true voltage-time function, whereas in the second, the oscillograph across  $AB$  records the voltage drop across the variable resistor. When the two traces are superimposed, the ratio of the

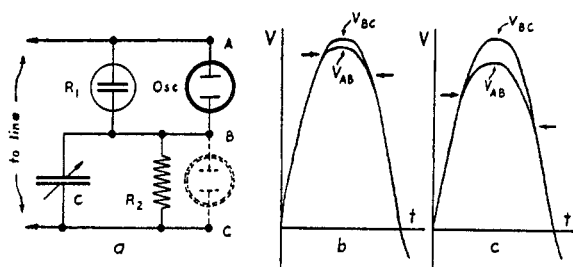


FIG. 5. a, Fucks' oscillograph arrangement; b and c, drawings of typical traces obtained by Fucks

ordinates measures directly the total resistance change of the solution. Figure 5b shows a result obtained with an aqueous sodium chloride solution, where the field effect is very small compared with the heat effect. The asymmetry of the trace  $V_{AB}$ , compared with the trace  $V_{BC}$  (indicated by horizontal arrows), shows clearly the heating of the solution during the time interval of  $10^{-6}$  sec.<sup>12</sup> The maximum field strength,  $E'_m$ , was 185 kilovolts per centimeter. A similar result for an aqueous solution of barium ferrocyanide, with  $E'_m = 180$  kilovolts per centimeter, is shown in figure 5c. Here the deviation from the true voltage-time function, and therefore the total resistance change, is much larger, although the heat effect is nearly the same as in the case of the sodium chloride solution

<sup>12</sup> If  $R_1$  showed only a field effect, the curve  $V_{AB}$  would be symmetrical with curve  $V_{BC}$ . The observed asymmetry is due to the heat effect, which is an integral function of time.

in figure 5b. This difference can be due only to an actual deviation from Ohm's law. Fucks' results are in excellent agreement with Wien's measurements. This agreement indicates that the method employed by Malsch and Wien to calculate the average potential of an oscillating discharge is correct.<sup>13</sup>

Already the early experiments indicated that the magnitude of the Wien effect increases with increasing valency of the ions. Wien (33) investigated a large number of salts of the valence types 1:1, 1:2, 1:3, 1:4, 2:1, 3:1, 2:2, 2:3, and 3:2 and found as an empirical rule that for the same average field strength and the same conductance at low fields,  $\lambda_{E=0}$ , the change in conductivity may be expressed by the equation

$$\Delta\lambda/\lambda_{E=0} = \text{constant} (z_1 z_2)^2 \quad (1)$$

This expression is only an approximation, and deviations as high as 20 per cent may occur for individual salts, especially those of the higher

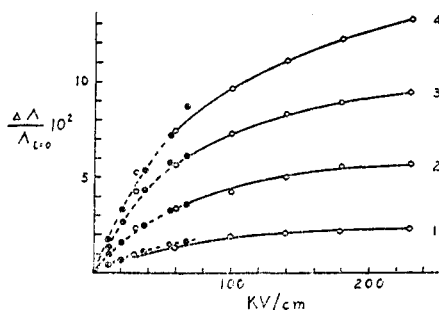


FIG. 6. Curve 1, lithium ferricyanide; curve 2, magnesium sulfate; curve 3, barium ferricyanide; curve 4, barium ferrocyanide. All for  $\lambda_{E=0} = 4.5 \times 10^{-5}$ . ● and ○ refer to results obtained with two different cells.

valence types. It is, however, very helpful in correcting relative measurements (as obtained with arrangements shown in figure 2) for the Wien effect of the comparison solution. Figure 6 illustrates the influence of valency on the observed conductance change for different salt types.

The dependence of the conductance change on the field strength is somewhat complicated. In figure 7 are shown idealized curves for three different valence types. Initially, at low fields, the curves are convex

<sup>13</sup> Hüter (12) later modified the method of Fucks in such a way that he was able to obtain photographic plots of instantaneous voltage *versus* current. He states that the oscillograph method is limited to an accuracy of about 1 per cent, mainly because it is very difficult to obtain a better concentration of the electronic beam. For more qualitative work, this method gives results much more rapidly than the integrating methods.

towards the axis of potential; they then pass through an inflection point where they approximate linearity and thereafter approach a constant limiting value. In the figure the different portions of the curves are indicated by continuous or broken lines. The limiting characteristic is to be seen also in figure 6, especially in the case of curve 1. How much of the

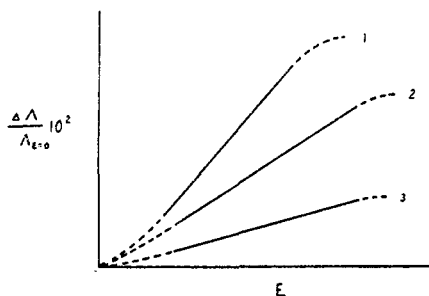


FIG. 7. Curve 1 represents a 2:4 salt type, curve 2 a 2:3 salt, and curve 3 a 1:3 salt

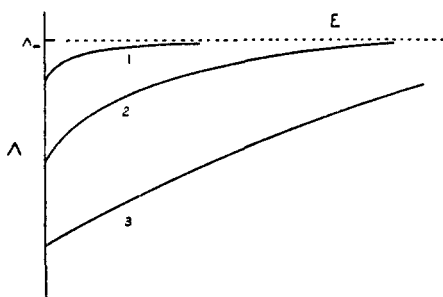


FIG. 8

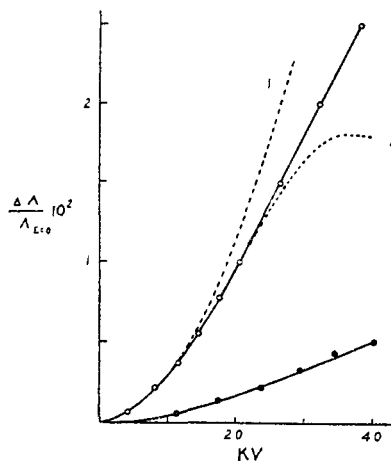


FIG. 9

FIG. 8. Curve 1 represents a very dilute solution, curve 2 a dilute solution, and curve 3 a moderately concentrated solution

FIG. 9. O, barium ferricyanide; ●, lithium ferricyanide

linear and limiting parts of the curves may be obtained experimentally depends upon concentration. In figure 8 the absolute values of conductivity are plotted against field strength for three concentrations. For solutions of high concentration, curve 3, the curve is nearly linear throughout, and it is not possible to obtain the limiting effect because of the breakdown of the solution. With solutions of lower concentration, curves

2 and 1, the curves are markedly concave toward the axis of potential; at lower fields the curves rise steeply and at higher fields they flatten out and approach a limiting value. The limit is the same at all concentrations, but this limit is reached at lower fields which are the lower, the lower the concentration.

The limiting effect is the most important result of these investigations. Wien showed that the equivalent conductance of a solution approaches a

TABLE 1  
*Limiting field effect and limiting concentration effect of several aqueous solutions*

SALT	$\nu_1:\nu_2$	10 <sup>c</sup>	$\frac{\Lambda_{E=\infty} - \Lambda_{E=0}}{\Lambda_{E=0}} 10^2$	$\frac{\Lambda_{\infty} - \Lambda_c}{\Lambda_c} 10^2$
K <sub>3</sub> Fe(CN) <sub>6</sub> .....	1:3	3.1	3.2	3.0
		6.4	4.3	4.3
Li <sub>3</sub> Fe(CN) <sub>6</sub> .....	1:3	3.7	3.7	3.6
		7.5	5.5	4.9
K <sub>4</sub> Fe(CN) <sub>6</sub> .....	1:4	2.9		4.7
		6.4	6.1	6.7
MgSO <sub>4</sub> .....	2:2	4.2	6.9	7.5
		8.9	9.0	10.7
MgCrO <sub>4</sub> .....	2:2	4.2	4.4	5.2
		8.7	7.4	7.2
Ba <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> .....	2:3	3.3	10.3	10.4
		7.2	14.2	15.0
Ba <sub>2</sub> Fe(CN) <sub>6</sub> .....	2:4	3.5	12.2	12.9
		7.7	19.8	19.4

limiting value as the field is increased indefinitely and that this limiting value is the same as that approached on diluting this solution indefinitely when the conductance is measured at low fields (33, 36, 37) (see, also, Schiele (30)). If  $\Lambda_c$  is the equivalent conductance of an electrolyte at ordinary fields, and  $\Lambda_{E=\infty}$  and  $\Lambda_{\infty}$  are, respectively, its limiting equivalent conductances as the field is increased indefinitely and as the concentration is decreased indefinitely, then  $\Lambda_{E=\infty} - \Lambda_c = \Lambda_{\infty} - \Lambda_c$ . In table 1 are given values of these differences each divided by  $\Lambda_c$ . As may be seen from

the table, these ratios are equal within the limits of the experimental errors involved in the measurements and the extrapolations. While the limiting field conductance thus agrees with the limiting concentration conductance, it is by no means certain that the two limiting values are identical; while the limiting concentration value is in most cases a close approximation, the limiting field value represents only a rough empirical extrapolation. In this connection attention may be called to Wilson's theory of the Wien effect, according to which a small electrophoretic effect remains at high fields.

In the light of these facts, it follows almost as a necessary conclusion that the high external field tends to decrease those influences which are responsible for the decrease of the ordinary low field conductance with increasing concentration.

The study of the convex part of the curve at low fields (figure 7) was especially difficult, because of the minute changes in conductance that had to be measured. It was therefore possible to study this portion of the curve only for salts of high valence type ( $z_1z_2 > 3$ ). Wien (35) used a relative method corresponding to that illustrated in figure 2. He corrected for the Wien effect in the comparison solution, which contained a 1:1 salt, in the manner described above, equation 1. The portion of the curve in question has nearly a quadratic form and may be expressed for fields up to 25 kilovolts per centimeter with the first two terms of the following series

$$\Delta\Lambda/\Lambda_{E=0} = AE'^2(1 - BE'^2 + \dots)$$

where the constants  $A$  and  $B$  are determined empirically. In figure 9 the experimental curve for barium ferricyanide is shown as a full line.<sup>14</sup> The dotted curves 1 and 2 are computed according to the above formula, using the first and the first and second terms, respectively.

Values of  $A$  and  $B$  obtained by Wien for aqueous solutions, by Bauer for solutions in acetone, and by Possner for a 50 per cent solution of cane sugar in water as a solvent are given in table 2.

The constants  $A$  and  $B$  are complicated functions of the temperature, the dielectric constant of the solvent, the valence of the ions, the concentration, the viscosity, and individual ionic properties. Generally, from the limited data available, it appears that  $A$  increases and  $B$  decreases with decreasing dielectric constant of the solvent. The values of Possner show that viscosity may have a slight influence on the observed results, although this effect is perhaps masked by the influence of the decreased dielectric constant.

<sup>14</sup> The experimental curve for lithium ferricyanide has been inserted to illustrate the influence of the valency of the ions upon the potential effect at low fields.

TABLE 2  
*Experimental values for A and B*

SALT	VALENCE TYPE	$\lambda_{E=0} \times 10^4$	$A \times 10^{11}$	$B \times 10^{11}$
Solvent, water. $T \sim 18^\circ\text{C}$ . (Wien (35))				
$\text{Li}_3\text{Fe}(\text{CN})_6$ .....	1:3	10.0	0.51	2.1
		5.0	0.68	2.3
		2.5	0.88	2.9
		1.25	0.96	3.8
$\text{Li}_4\text{Fe}(\text{CN})_6$ .....	1:4	10.0	0.91	1.5
		5.0	1.57	2.1
		2.5	2.00	2.3
$\text{MgSO}_4$ .....	2:2	10.0	1.11	1.7
		5.0	1.49	1.7
		2.5	1.96	2.3
		1.25	2.50	6.0
$\text{Ba}_3[\text{Fe}(\text{CN})_6]_2$ .....	2:3	10.0	2.6	1.9
		5.0	3.9	2.1
		2.5	5.1	4.5
		1.25	5.6	7.5
$\text{Ba}_2\text{Fe}(\text{CN})_6$ .....	2:4	10.0	4.2	1.9
		5.0	5.0	3.2
		2.5	10.9	3.9
Solvent, acetone. $T \sim 18^\circ\text{C}$ . (Bauer (1))				
KI.....	1:1	8.0	0.263	0.0527
		4.0	0.334	0.0527
		2.0	0.334	0.0438
$\text{CdI}_2^*$ .....	2:1	8.0	0.387	0.0351
		4.0	0.615	0.0438
		2.0	0.720	0.0351
$\text{Cd}(\text{NO}_3)_2^*$ .....	2:1	8.0	0.211	0.0438
		4.0	0.527	0.0438
		2.0	0.720	0.0351
$\text{Ni}(\text{NO}_3)_2^*$ .....	2:1	8.0	0.176	0.0527
		4.0	0.438	0.0351
		2.0	0.527	0.0140
Solvent, 50 per cent aqueous solution of cane sugar. $D \sim 60$ . $18^\circ\text{C}$ . (Possner (27))				
$\text{MgSO}_4$ .....	2:2	0.23	1.8	7.4

\* These electrolytes are probably not completely dissociated in acetone and thus may exhibit a small dissociation field effect superimposed on the first Wien effect.



While the specific properties of the solution and the temperature influence the magnitude of the Wien effect, it is also dependent upon the length of the time interval during which the field is applied. In table 3 are given values of  $\Delta\Lambda/\Lambda_{E=0}$  for three salts for time intervals varying from  $6 \times 10^{-7}$  to  $5 \times 10^{-5}$  sec., the average potential being the same for all time intervals. On examining the table it is seen that in all cases the value of  $\Delta\Lambda/\Lambda_{E=0}$  increases initially with increasing length of the time interval and approaches what appears to be a constant limiting value, this limit lying at longer time intervals in the case of salts of higher valence type. Thus for beryllium sulfate  $\Delta\Lambda/\Lambda_{E=0}$  has reached a constant value of 1.08 for a time interval of  $1.4 \times 10^{-6}$  sec., while for calcium ferrocyanide a constant value of 10.5 is reached for a time interval of  $1.5 \times 10^{-5}$  sec. This interesting effect has not yet been the subject of a detailed investigation. It has been studied only sufficiently to determine the length of the

TABLE 3

*The influence of the impulse duration,  $\tau$ , on the Wien effect for a constant average potential (33)*

$\tau$	$(\Delta\Lambda/\Lambda_{E=0}) \times 10^2$		
	BeSO <sub>4</sub>	Ca <sub>2</sub> Fe(CN) <sub>6</sub>	Ba <sub>2</sub> Fe(CN) <sub>6</sub>
<i>seconds</i>			
$6 \times 10^{-7}$	0.92		
$9 \times 10^{-7}$	0.99	4.8	
$1.4 \times 10^{-6}$	1.08	6.8	8.6
$4.5 \times 10^{-6}$	1.04	8.4	10.9
$1.5 \times 10^{-5}$	1.03	10.5	13.1
$3.0 \times 10^{-5}$	1.15	10.5	12.9
$5.0 \times 10^{-5}$	1.07	10.7	13.1

impulse duration necessary to render the observed field effect independent of the length of this impulse duration.<sup>15</sup>

Summarizing the outstanding phenomena that characterize the Wien effect, we have: (1) The conductance of a strong electrolyte increases with increasing field strengths and approaches a limiting value which appears to be identical with  $\Lambda_{\infty}$ . With decreasing concentration this limit is approached at lower fields. (2) The magnitude of the field effect increases with increasing valency of the ions. (3) For very low fields and to a first approximation the conductance increase is proportional to the square of the field, the proportionality constant depending upon the nature of the solute and the solvent. (4) The conductance increase is a function of

<sup>15</sup> This effect led Debye and Falkenhagen (5) to the theoretical prediction of the dispersion phenomena in electrolytic solutions at high frequencies with ordinary potentials.

the impulse duration and for 2:4 salts approaches a constant value for  $\tau > 10^{-5}$  sec.; for salts of lower valence type constancy is reached at lower periods.

### C. The dissociation field effect

During investigations incident to the development of high electrolytic resistances, Gyemant (11) studied solutions of picric acid in benzene-alcohol mixtures. In the course of these investigations he found that the addition of phenol or mineral oils reduces the temperature coefficient of conductance of these solutions to zero. On measuring the resistance of these solutions under high potentials, he observed deviations from Ohm's law which were far greater than any deviations previously observed by Wien and his coworkers. Because of the fact that the temperature coefficient was zero and  $\lambda_{E=0}$  was less than  $10^{-8}$  mhos, he determined the resistance by simultaneously measuring voltage and current. Thus, at a field strength of 42 kilovolts per centimeter, he found that for a 0.7 per cent picric acid solution in benzene containing 5 per cent ethyl alcohol and 0.4 per cent mineral oil,  $\Delta\lambda/\lambda_{E=0}$  was equal to 0.85, and for a 0.7 per cent picric acid solution in benzene containing 8 per cent ethyl alcohol and 3 per cent mineral oil,  $\Delta\lambda/\lambda_{E=0}$  was equal to 0.52. Deviations of this magnitude have not been observed in aqueous solutions. Furthermore, the conductance of these solutions was found to be a linear function of the field strength.

In order to account for these enormous deviations, Gyemant considered it possible that the degree of dissociation might be increased by high fields. As an *experimentum crucis* he measured the conductance perpendicularly to the high field, reasoning that if the degree of dissociation increases with field strength, the conductivity measured in this direction should increase proportionally to the conductance increase in the direction of the high field. Since the results of this experiment were negative, he concluded that the observed high field effect was probably not due to an increase of dissociation.

Joos (13), relying upon this experiment, suggested that the mechanism might be the same as for the first Wien effect, i.e., a property of free ions only. To clarify this question, Wien (38) and Schiele (28) studied the deviations of strong and weak acids in aqueous solution under the influence of high fields.

These electrolytes were chosen because it had been observed that their solutions exhibit dispersion effects of the same magnitude in high-frequency fields. Both the Debye-Falkenhagen dispersion effect and the first Wien effect are due to interactions between free ions and field. If, therefore, the field effects in strong and weak acids are to be accounted for on the

basis of free ions only, then the magnitude of these effects as observed should be of the same order. If, however, they were found to be of different order, this would indicate that different mechanisms are involved in the effect of fields on strong and weak acids.

Schiele, using an improved baretter method, compared acetic acid and the chloroacetic acids with hydrochloric acid. The dissociation of these acids increases with increasing number of substituent chlorine atoms, and Schiele found that the differences in the conductance change between the acids and hydrochloric acid increase as the carboxylic acid is weaker.

The results of Schiele's investigations are shown in figure 10b, where values of differential conductance effects,  $\Delta\Lambda/\Lambda_{E=0}$ , are plotted against field strength. Trichloroacetic acid, being a strong acid, shows no observable difference with respect to hydrochloric acid. With dichloroacetic acid (curve 1) a difference is just observable. Monochloroacetic acid

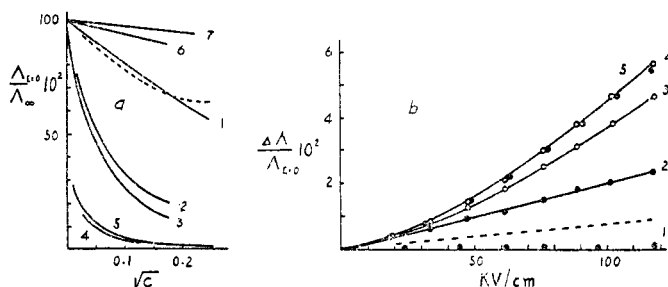


FIG. 10. Curve 1, dichloroacetic acid; curve 2, chloroacetic acid; curve 3, tartaric acid; curve 4, propionic acid; curve 5, acetic acid; curve 6, trichloroacetic acid; curve 7, hydrochloric acid; ----, sulfuric acid. In b,  $\lambda_{E=0} = 2.0 \times 10^{-4}$ ; compared against hydrochloric acid.

(curve 2) shows a large effect and acetic acid (curve 5) a very large one. The curve for propionic acid, which has practically the same strength as acetic acid, lies just below that of the latter acid (curve 4). The curve for tartaric acid lies well below that of acetic acid, which is in accord with the greater strength of tartaric acid. In figure 10a are shown the values of  $\Delta\Lambda_{E=0}/\Lambda_{\infty}$  for a number of acids. Comparing with figure 10b it is apparent that acids having a low conductance exhibit a high field effect.

The bases exhibit field effects closely paralleling those of the acids. Strong bases exhibit no difference with respect to hydrochloric acid, while weak bases exhibit an effect which is the greater the weaker the base. The effects are illustrated in figure 11.

Solutions of normal salts in solvents of lower dielectric constant in which the electrolyte is incompletely dissociated exhibit the same effect as do

weak acids and bases in water. In figure 12 are shown curves for potassium iodide and lithium bromide in acetone. Potassium iodide is a much stronger electrolyte in this solvent than is lithium bromide, as appears from figure 12a. As may be seen from figure 12b, potassium iodide exhibits a much smaller differential effect than does lithium bromide.

The results just described show conclusively that the magnitude of the field effect increases with decreasing strength of the electrolyte, that is, with increasing association of the ions to ion pairs. Since the large observed increase in conductance cannot be accounted for by the first Wien effect, it is impossible to escape the conclusion that the enhanced effect found in the case of weakly dissociated electrolytes is due to an increased dissociation of the electrolyte under the action of the applied field.

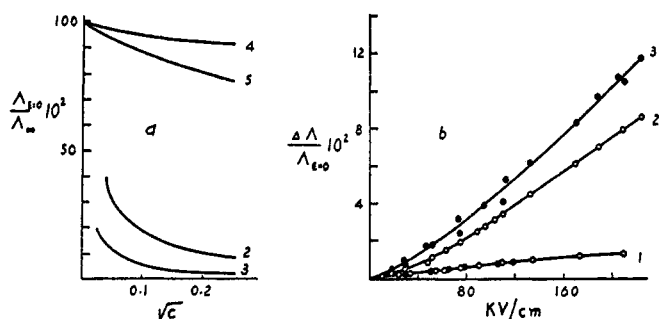


FIG. 11. Curve 1, ●, barium hydroxide, ○, sodium hydroxide; curve 2, methylamine; curve 3, aqueous ammonia; curve 4, sodium hydroxide; curve 5, barium hydroxide. In b,  $\lambda_{E=0} = 2.0 \times 10^{-4}$ ; compared against hydrochloric acid.

Although the first and the second Wien effects cannot be accounted for by the same mechanism, they, nevertheless, have certain characteristics in common. As in the case of the first Wien effect, the change in conductivity for constant field in the second Wien effect is a function of the impulse duration. Results of Michels (21) for cobalt chloride in acetone are shown in figure 13, from which it is seen that for this electrolyte the effect approaches a constant value for the impulse duration  $\tau > 1.7 \times 10^{-6}$  sec.

For low fields, plots of  $\Delta\Lambda/\Lambda_{E=0}$  against  $E'$  for the dissociation field effect are slightly convex toward the  $E'$ -axis, in which respect they resemble the curves of the first Wien effect. On the other hand, no trend toward a limiting effect has been observed in the case of the dissociation field effect. Recalling the  $\Lambda_{E=0}/\Lambda_{\infty} - \sqrt{c}$  curves, it is apparent that the dissociation field effect yields only a relatively small increase in the number of free ions at 100 kilovolts per centimeter in the aqueous solutions measured.

Consequently, an extremely high external field would be necessary to dissociate these electrolytes completely;<sup>16</sup> it seems very doubtful that such fields are actually attainable.

In this connection it is of interest to mention the studies of Malsch and Hartley (18) of colloidal solutions of cetylpyridonium chloride in water,

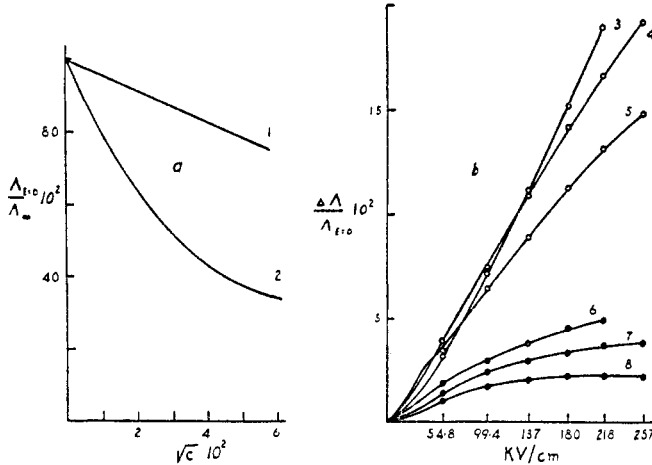


FIG. 12. Acetone solutions of potassium iodide (curves 1, 6, 7, and 8) and of lithium bromide (curves 2, 3, 4, and 5), where in curve 3  $\lambda_{E=0} = 0.00012$  and  $c = 0.00168$ ; in curve 4  $\lambda_{E=0} = 0.00006$  and  $c = 0.00058$ ; in curve 5  $\lambda_{E=0} = 0.00003$  and  $c = 0.00023$ ; in curve 6  $\lambda_{E=0} = 0.00012$  and  $c = 0.00073$ ; in curve 7  $\lambda_{E=0} = 0.00006$  and  $c = 0.00036$ ; and in curve 8  $\lambda_{E=0} = 0.00003$  and  $c = 0.00017$ .

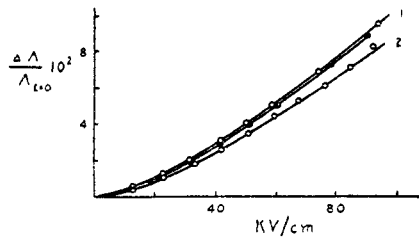


FIG. 13. Acetone solution of cobalt chloride where  $\lambda_{E=0} = 0.93 \times 10^{-4}$ . In curve 1,  $\circ$ ,  $\tau = 3.6 \times 10^{-6}$ ;  $\bullet$ ,  $\tau = 1.9 \times 10^{-6}$ . In curve 2,  $\tau = 5.4 \times 10^{-7}$ .

where very large potential effects were observed. The outstanding result is that the conductance for very high fields does not approach but exceeds the value of  $\Lambda_{\infty}$  (figure 14). Malsch and Hartley give the following ex-

<sup>16</sup> It must be remembered that the presence of any free ions leads to an ion atmosphere and thus to a deviation explained by the first Wien effect.

planation: When sufficiently concentrated, the solution contains very large complexes of positive ions (micelles), with some small negative ions relatively firmly attached to these complexes, thus decreasing their mobility and consequently the low field conductance. High fields, however, tend to separate the anions from the large complexes, thus leaving very highly charged positive particles. According to Stokes' law the contribution to the conductance of a complex is larger than that of a corresponding number

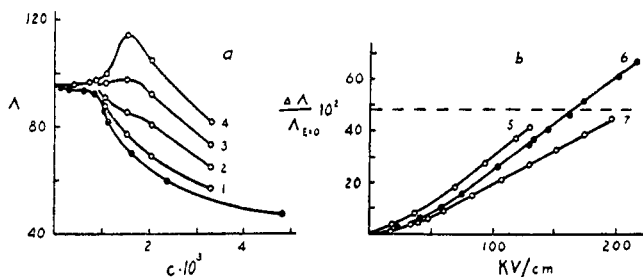


FIG. 14. Cetylpyridonium chloride in water. In a: ●, low potential; curve 1, 50 kilovolts per centimeter; curve 2, 100 kilovolts per centimeter; curve 3, 150 kilovolts per centimeter; curve 4, 200 kilovolts per centimeter;  $\tau = 8 \times 10^{-7}$  sec. In b: ---- is  $\Delta\Lambda/\Lambda_{E=0}$  for  $\Lambda = \Lambda_{\infty}$ ;  $\lambda_{E=0} = 1.29 \times 10^{-4}$ ; curve 5,  $\tau = 16 \times 10^{-7}$  sec.; curve 6,  $\tau = 8 \times 10^{-7}$  sec.; curve 7,  $\tau = 2 \times 10^{-7}$  sec.

of single ions, so that the conductance may well increase to a value which is larger than  $\Lambda_{\infty}$ .<sup>17</sup>

### III. THEORY

Many of the more important properties of electrolytes depend upon ion interaction due to Coulomb forces, which represent the extreme case of a "chemical force" that falls off the most slowly of all forces leading to an interaction. The theoretical analysis of accurate experimental data has

<sup>17</sup> Since the writing of this review, H. Diekmann (Ann. Physik [5]32, 378 (1938)) has published results of an investigation of aqueous solutions of cetylpyridonium chloride and of magnesium sulfate in glycerol-water mixtures at different temperatures. The same effect that is found for cetylpyridonium chloride is also present in systems of magnesium sulfate-glycerol-water. Diekmann therefore draws the conclusion that there is a certain micelle structure in the case of the magnesium sulfate-glycerol-water systems. However, it may be pointed out that: (1) Ordinary conductance data for magnesium sulfate-glycerol-water systems do not show the behavior typical of colloid electrolytes. (2) For the relatively high concentrations studied and for a 2:2 salt in a solvent of  $D \sim 60$ , relatively strong ionic association must be expected. (3) Diekmann does not mention that the high-field conductance exceeds  $\Lambda_{\infty}$ , as it does in the case of cetylpyridonium chloride solutions in water.

led to a theory of electrolytes where long-range interactions play a rôle in accounting for the properties of completely dissociated electrolytes, while short-range interactions<sup>18</sup> are an important or determining factor in the case of incompletely dissociated electrolytes. By careful selection of experiments and conditions, various characteristics of these forces become known. Conductance studies, using external fields of low potential and low frequency, of high potential and of high frequency, have been very successful in yielding data which have been theoretically interpreted by using these interactions as the basis of analysis. However, that we know very little about the characteristics of these interactions is apparent when it is recalled that only data for extremely dilute solutions may be accounted for and that even here discrepancies appear.

The Debye-Hückel-Onsager theory of conductance (6, 22) is based on the assumption that only a stationary field of very low potential ( $E \sim 0$ ) is being applied when the conductance is measured. Under these conditions, approximations may be made in which terms containing higher powers of the field are neglected. This leads to an equation in which the conductance does not depend upon the field,—a result which has been amply verified by experiment. Obviously this theory must be modified if it is to account for the first Wien effect, which is observed when the solution is subjected to a high field. As a first attempt in this direction, Joos and Blumentritt (3, 4, 14) evaluated the neglected higher terms of the Debye-Hückel-Onsager equation. They obtained an equation of the form

$$\Delta\Lambda/\Lambda_{E=0} = AX^2 - B'X^4 + \dots$$

This result guided Wien in his investigation of the low-potential region (37). Unfortunately, Joos and Blumentritt made assumptions as a result of which their theory has only a qualitative significance (39). Furthermore, it fails to account for the limiting effect obtained with very high fields.

Using another approach, Falkenhagen (7) later obtained a qualitative theory which applied to the whole curve. His treatment leads to the limiting effect and shows, in general, the influence of valence and dielectric constant. Basing their calculations upon this theory, Falkenhagen and Fleischer (8) introduced the non-stationary field, thus obtaining an equation which shows the dependency of the Wien effect upon frequency.

Overcoming the mathematical difficulties involved, Wilson (39) developed a quantitative theory of the first Wien effect which is applicable to the whole curve; for very low fields the Wilson conductance equation reduces to the quadratic form obtained by Joos and Blumentritt.

<sup>18</sup> Short-range interactions may involve quantum as well as Coulombic forces.

In the case of the dissociation field effect, a different approach must be adopted, since there is no longer complete dissociation, but rather association with an equilibrium existing between ion pairs and free ions. As explained above, the phenomenon of the dissociation field effect was thought to be due to increased dissociation. Onsager (23) showed that while the rate of formation of ion pairs is independent of the field, the rate of dissociation of ion pairs is a function of the field. This analysis indicates that the increased dissociation due to the field is independent of the stoichiometric concentration.

Even though the concepts of ion interaction had been well established in the theory of electrolytes, the extension of the theory to the Wien effect constitutes a major advance in the attack on the general problem of ionic solutions.<sup>19</sup> To review briefly the modern concepts underlying the theory of ionic solutions, we shall first consider the case in which the electrolyte is completely dissociated. The electrostatic attractions and repulsions between the ions do not permit a perfectly random distribution of the ions; on the time average, there will be more ions of unlike sign than of like sign in the neighborhood of the given ion. This "ion atmosphere," as it is called, has a symmetrical distribution when no external field acts. One of the characteristics of this atmosphere is that it has a finite "time of relaxation," i.e., it does not disappear immediately when the central ion is removed, and *vice versa*. Consequently, when a stationary field of very low potential is applied, causing the central ion to move, the distribution of the ion atmosphere becomes asymmetric; there are more ions of like sign in front and unlike sign behind the central ion than in the case of the symmetrical distribution. The "relaxation force" due to asymmetry of the ion atmosphere has a retarding effect upon the motion of the central ion.

There is still another retarding effect acting upon the moving ion, commonly referred to as the "electrophoretic" effect or hydrodynamical effect. According to hydrodynamic laws, moving ions carry solvent with them. This effect extends for some distance from the central ion, so that the ion atmosphere again influences the motion of the central ion. The hydrodynamical effect manifests itself in such a way that the ion is not moving in a stationary solvent, but rather in one that is moving in the opposite direction. These two retarding effects have been incorporated in the Debye-Hückel-Onsager theory of ordinary conductance and account satisfactorily for the decrease of conductance with increasing concentration, in the limiting case of low concentrations.

<sup>19</sup> For a detailed exposition of the theory of electrolytes we refer the reader to the monograph by Falkenhagen (Falkenhagen: Elektrolyte, Hirzel, Leipzig (1932); Electrolytes, Oxford University Press, Oxford (1934); Electrolytes, Alcan, Paris (1934)).



If we apply a very high potential to a solution, we find that the ions are given enormous velocities as a result of which the ion atmosphere is very greatly modified. However, as Wilson shows, in the limit of extremely high fields the ion atmosphere again becomes symmetrical but now contains ions of like sign, ions of unlike sign being constantly swept away at such a rate that the field of the ion in question does not influence the distribution of ions of opposite sign. Thus the relaxation force disappears, leaving only a small contribution from the electrophoretic effect.

Secondly, we shall consider "weak" electrolytes, or "strong" electrolytes in solvents of low dielectric constant. For such systems<sup>20</sup> the energy due to short-range interactions between the ions of unlike sign is great enough, compared with the energy of thermal agitation, so that, on the time average, the two ions spend more time as a *pair* than as *free* ions. In other words, the number of ions free to conduct the electric current is small in comparison with the number of ion pairs that have the properties of dipoles. Bjerrum (2) and Fuoss and Kraus (10) have given a satisfactory theory of ionic association which, when combined with the Debye-Hückel-Onsager theory, accounts for the conductance of dilute solutions at low fields. When a high field is applied, two effects come into play: the free ions give rise to a small, normal Wien effect, while the ion pairs undergo increased dissociation in accordance with Onsager's theory of the influence of the field in the dissociation process. In the latter case the high field has shifted the equilibrium, *ion pairs*  $\rightleftharpoons$  *free ions*, to the right, thus increasing the number of ions free to carry the current. Making a study of this shift in equilibrium, Onsager was able to obtain an equation which is in quantitative agreement with the experimental values.

#### A. Theory of the first Wien effect

##### 1. The Joos-Blumentritt theory for small fields

Joos and Blumentritt in their first papers (3, 14) calculated the higher terms in the field strengths from the original Debye-Hückel theory (6) and obtained

$$\Delta\Lambda/\Lambda_{E=0} = AX^2 - B'X^4 + \dots$$

where  $A$ ,  $B'$ ,  $\dots$  are known constants. In the later paper by Blumentritt (4) these calculations were repeated, using the modified theory of Onsager (22). The values of these constants are in fair agreement with the experimental values. However, perfect agreement is not possible because Joos and Blumentritt used symmetry conditions which are valid only for zero field. Since it is possible to reduce Wilson's theory to the above form for

<sup>20</sup> We are now considering those systems on the other extreme where  $\alpha \ll 1$ . There is an intermediate type where  $\alpha$  is less than unity, yet is large enough so that the number of free ions is comparable with the number of ions in ion pairs.

low fields, it is not necessary to consider the Joos-Blumentritt theory in detail.

## 2. The Falkenhagen theory for the complete curve

Under high fields an ion has such a high velocity that it travels through many thicknesses of the ion atmosphere,  $1/\kappa$ , during a time interval,  $2\Theta$ , which is the time necessary for the ion atmosphere to reach a random distribution after the removal of the central ion. Thus, in the case of high fields, the normal ion atmosphere is not formed. It is of interest to calculate the number of ion atmosphere diameters that an ion travels in a high field. This has been done by Falkenhagen (7).

If an  $i$  ion with a charge  $z_i e = e_i$  moves with a velocity  $v_i$  against a frictional resistance  $\rho_i$  under a field  $E$ , we have

$$v_i = z_i e E / \rho_i = 0.1033 \times 10^{-4} E' l_i / z_i \text{ cm. per second}$$

where  $E'$  is the field in volts per centimeter and  $l_i$  is the mobility of the ion. If we now multiply  $v_i$  by  $2\Theta$ , we have the distance the ion travels in  $2\Theta$  sec. Furthermore, by dividing this distance by  $1/\kappa$ , we obtain the distance travelled in terms of the diameter of the ion atmosphere, namely,

$$\kappa s_i = 0.207 \times 10^{-4} E' l_i \Theta \kappa / z_i$$

If we now consider a  $10^{-4}$  molar aqueous solution of potassium chloride, we have, for  $18^\circ\text{C}$ ,

$$l_1 = l_2 = 65 \text{ ohms}^{-1} \text{ cm.}^2$$

$$\Theta = (0.553/c') \times 10^{-10} \text{ sec.}$$

$$1/\kappa = (3.06/\sqrt{c'}) \times 10^{-8} \text{ cm.}$$

and for  $E' = 100$  kilovolts per centimeter we obtain

$$\kappa s_i = 24.4$$

According to this example, then, the time during which a given ion is under the influence of an oppositely charged ion is only one twenty-fifth of the relaxation time, or, in other words, the time during which a given ion is in the neighborhood of other oppositely charged ions is so short that the distribution of the latter remains uninfluenced because of the relaxation effect. The above computation is, of course, only a rough approximation, since it involves assumptions including one such that the relaxation force is proportional to the field, an assumption which does not lead to a limiting effect.

Let us now consider the dependency of the relaxation force upon the external field. We will simplify the problem by neglecting the Onsager

corrections for the influence of the Brownian movement, as well as the electrophoretic effect and its influence upon the relaxation force, and we will further assume that the ions of the electrolyte have equal charge and have the same mobility. Thus the application of this theory is limited as well as approximate.

The equation of continuity yields

$$\frac{dn_i}{dt} = \operatorname{div} \mathbf{v}_i n_i = \operatorname{div} \left( \frac{kT}{\rho_i} \operatorname{grad} n_i - \frac{n_i \mathbf{K}}{\rho_i} \right) \quad (2)$$

where  $n_i$  is the time average of the number of  $i$  ions per cubic centimeter, and  $\mathbf{K}$  is the force acting upon the ions. Let us now change our variables so that the origin of the coördinate system is at the center of the  $i$  ion and moves with it, with a velocity  $v$  parallel to the  $X$ -axis, so that  $x = X - vt$ ,  $y = Y$ ,  $z = Z$ ,  $t = t'$ ,

$$\frac{dn_i}{dt} = -v \frac{\partial n_i}{\partial x} + \frac{\partial n_i}{\partial t'}$$

For the stationary case where  $\partial n_i / \partial t' = 0$ , and substituting for  $\mathbf{K}$  its value  $e_i \mathbf{E} - e_i \operatorname{grad} \psi$ , equation 2 becomes

$$-v \frac{\partial n_i}{\partial x} = \operatorname{div} \left\{ \frac{kT}{\rho_i} \operatorname{grad} n_i + \frac{n_i e_i}{\rho_i} \operatorname{grad} \psi \right\} \quad (3)$$

The potential  $\psi$  is satisfied by the Poisson equation,

$$\Delta \psi = -\frac{4\pi}{D} \sum e_i n_i$$

A further simplification of equation 3 may be effected by introducing for  $n_i$  the value  $\bar{n}_i + \nu_i$ , where  $\bar{n}_i$  is the concentration for random distribution and  $\nu_i$  the perturbation caused by the acting forces. Thus

$$\Delta \nu_i + \frac{\rho_i v}{kT} \frac{\partial \nu_i}{\partial x} = -\frac{n_i e_i}{kT} \Delta \psi \quad (4)$$

where

$$\Delta \psi = -\frac{4\pi}{D} \sum e_i \nu_i$$

For the simple case of an electrolyte having ions of equal charge and equal mobility, we have

$$e_1 = -e_2 = e, \quad n_1 = n_2 = n, \quad \rho_1 = \rho_2 = \rho$$

Letting

$$\nu_1 = -\nu_2 = -\frac{ne}{kT} f, \quad \kappa^2 = \frac{8\pi ne^2}{DkT},$$

and

$$2\mu = \frac{\rho v}{kT} = \frac{eE}{kT}$$

equation 4 becomes

$$\Delta f + 2\mu \frac{\partial f}{\partial x} = \Delta\psi \quad (5)$$

where  $\Delta\psi = \kappa^2 f$ . Equation 5 may be written in the two forms

$$\Delta f - \kappa^2 f + 2\mu \frac{\partial f}{\partial x} = 0 \quad (6)$$

$$\Delta \left( \Delta\psi - \kappa^2 \psi + 2\mu \frac{\partial \psi}{\partial x} \right) = 0 \quad (7)$$

The distribution function  $f$  which satisfies equation 6 and the boundary condition is

$$f = C' \frac{\exp(-\mu x) \exp(-\sqrt{\kappa^2 + \mu^2} r)}{r}$$

where  $r$  is the radial distance from the central ion. To evaluate  $C'$ , we let  $\mu = 0$  so that

$$(f)_{\mu=0} = C' \frac{\exp(-\kappa r)}{r} \quad (8)$$

When  $\mu = 0$ , the above equations lead to the original Debye-Hückel expression in which Ohm's law is valid.

In order to obtain  $C'$  from equation 8 we recall that for a space charge density  $P$ ,

$$\Delta\psi = -\frac{4\pi}{D} P$$

and

$$f = -\frac{4\pi}{D} \frac{P}{\kappa^2} \quad (9)$$

Consequently, for  $(f)_{\mu=0}$ ,

$$(f)_{\mu=0} = -\frac{4\pi P^0}{D\kappa^2} = +\frac{\Delta\psi^0}{\kappa^2} = +\frac{e \exp(-\kappa r)}{Dr}$$

and

$$C' = e/D$$

so that

$$f = \frac{e}{Dr} \exp(-\mu x - \sqrt{\kappa^2 + \mu^2} r) \quad (10)$$

This expression gives the charge density distribution as a function of  $x$  and  $r$ . What we are now interested in is the force, in the  $x$ -direction, due to this distribution. This force is obviously

$$K_R = \frac{e}{D} \iiint \frac{P}{r^2} \cos \theta \, dV$$

With equations 9 and 10 we may reduce the above expression to

$$K_R = -\frac{e^2 \kappa^2}{2D} \int_{-\pi/2}^{\pi/2} \int_0^\infty \frac{\exp(-\mu r \cos \theta - \sqrt{\mu^2 + \kappa^2} r)}{r} \sin \theta \cos \theta \, d\theta \, dr \quad (11)$$

and integrating, we obtain

$$K_R = -\frac{e^2 \kappa^2}{D} \left( \frac{w}{2} - \frac{w^2 - 1}{4} \ln \frac{w + 1}{w - 1} \right) = -\frac{e^2 \kappa^2}{D} y$$

where  $w^2 = 1 + \frac{\kappa^2}{\mu^2}$ .

In order to study the dependency of  $y$  upon  $\mu/\kappa$ , we will let  $u = (\mu/\sqrt{c'}) \times 10^{-7}$ . Plotting  $y$  against  $u$ , we obtain a curve through the origin which approaches  $y = 0.5$  asymptotically as  $u \rightarrow \infty$ . This means that, for infinite field,  $K_R = -e^2 \kappa^2 / 2D$ . Since  $u$  is proportional to  $E$ , we see that a decrease in  $\sqrt{c'}$  acts in the same way as an increase in the external field. This is in agreement with the results shown graphically in figure 8.

In order to obtain the conductance in any field, we apply the equation  $e\mathbf{E} - \rho\mathbf{v} + \mathbf{K}_R = 0$ , so that

$$\lambda = \frac{2ne^2}{\rho} - \frac{2e^3 \kappa^2 n}{\rho DE} y \quad (12)$$

where  $2ne^2/\rho = \lambda_\infty$ . Since Falkenhagen found it inconvenient to proceed further in an explicit form, he tabulated the functions necessary for calculating the change of conductance with field.

By numerical calculation it may thus be shown that  $\lambda_\infty$  is approached as a limit at high fields. At lower concentrations this limit is approached at lower fields. Other characteristics of the Wien effect follow from the theory: Increasing the temperature displaces the curves toward higher field strength; a similar shift occurs on decreasing the dielectric constant of the solvent.<sup>21</sup> The theory accounts for the influence of valency on the field effect, in qualitative agreement with experiment.

<sup>21</sup> Care should be observed in selecting the system to be studied. Solutions in which ion association occurs should be avoided, since such solutions exhibit the second Wien effect. For example, Bauer's results in acetone seem to be in agreement with the first Wien effect (potassium iodide, for example) and they may well be measurably influenced by ion association. In the case of lithium bromide in acetone the influence of ion association is evident.

As has already been pointed out, all these effects are dependent upon the relaxation time  $\Theta$ , which decreases with increasing concentration, with increasing temperature, and with decreasing dielectric constant. It is worth while to mention that because of these characteristics of  $\Theta$ , the Wien effect is closely related to the Debye–Falkenhagen dispersion effect.

### 3. The Falkenhagen–Fleischer theory for the frequency dependence of the Wien effect<sup>22</sup>

Debye and Falkenhagen (5) developed their dispersion theory of electrolytes at low fields by introducing the frequency into the Debye–Hückel–Onsager theory which relates to stationary low fields. In a similar manner, Falkenhagen and Fleischer (8) introduced the frequency into the Falkenhagen theory for stationary high fields as outlined above and thus developed a theory of electrolytes for non-stationary high fields. In so doing, equation 6 has the complex term  $\kappa^2(1 + i\omega\Theta)$  instead of just  $\kappa^2$ . This leads to a differential equation which Falkenhagen and Fleischer have solved, giving

$$\frac{\Delta\Lambda}{\Lambda_{E=0}} = \frac{e^2\kappa^2}{2DkT\mu} y' \quad (13)$$

where the symbols have the same significance as in the preceding theory.  $y'$ , which is the real part of a certain function,<sup>23</sup>  $y^*$ , is a very complicated expression, which Falkenhagen and Fleischer have expressed in tabular instead of explicit form. Their table contains the real part of  $y^*$  as a function of  $\mu\sqrt{DT/c'}$  and  $\omega\Theta$ . In figure 15 are shown curves of  $y'$ , the real part of  $y^*$ , plotted against  $\omega\Theta$  with  $\mu\sqrt{DT/c'} \times 10^{-9}$  as a parameter.

Taking the qualitative nature of their theory into account, Falkenhagen and Fleischer conclude that their results are in good agreement with the experimental results of Bauer and Michels. However, the experimental material is so meager that a thoroughgoing comparison between theory and experiment is not now possible. It would seem of interest to study the frequency deviation of the Wien effect under conditions of field and frequency that correspond to the maximum in the  $y'-\omega\Theta$  plot.

### 4. The Wilson theory for binary electrolytes

In formulating his theory Wilson (39) obtained complicated systems of differential equations which he was able to solve and which give a complete

<sup>22</sup> Falkenhagen (8) announces a future publication in which he will consider the theoretical treatment of the influence of high fields upon the dielectric constant of the solution. Experimental studies of this phenomenon have not been made as yet and will meet extreme experimental difficulties, at least for solutions of high conductance.

Since the writing of this review, this theory has been published by F. Frölich (Physik. Z. 40, 124 (1939)).

<sup>23</sup> Falkenhagen and Fleischer do not give the function  $y^*$  in their publication.

account of the first Wien effect. The solution that Wilson obtained is valid for low-frequency conductance phenomena of binary electrolytes in any field. According to this theory the limiting conductance does not reach  $\Lambda_\infty$ , since only the relaxation force disappears completely, leaving a small contribution due to the electrophoretic effect.

In attacking this problem Wilson proceeded in the familiar way by considering a solution containing per cubic centimeter  $n_1, n_2, \dots, n_s$  ions of species 1, 2,  $\dots, s$  with charges  $e_1, e_2, \dots, e_s$  E.S.U., and two elements of volume  $dV_1$  and  $dV_2$  located by a vector  $\mathbf{r}$  drawn between them. Considering the time average concentrations of the  $j$  ion and  $i$  ion in the two elements of volume  $dV_1$  and  $dV_2$ , respectively, it is possible to show<sup>24</sup> that

$$f_{ji}(\mathbf{r}) = n_j n_{ji}(\mathbf{r}) = n_i n_{ij}(-\mathbf{r}) = f_{ij}(-\mathbf{r}) \quad (14)$$

where  $n_{ji}(\mathbf{r})$  is the time average concentration of the  $i$  ions in  $dV_2$  while a  $j$  ion is in  $dV_1$ , and  $n_{ij}(-\mathbf{r})$  that of the  $j$  ions in  $dV_1$  while an  $i$  ion is in

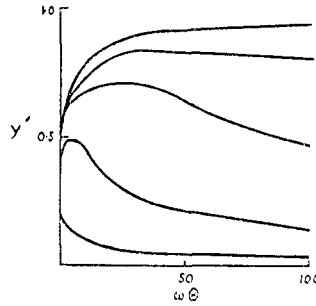


FIG. 15.  $y'$  against  $\omega\Theta$ , where the parameter  $\frac{eE}{2kT} \sqrt{\frac{DT}{c'}}$   $\times 10^{-9} = 4, 16, 47, 109,$  and 1550 (from the bottom up, respectively)

$dV_2$ . The equations of continuity, in terms of these distributions, are, for the steady state of the solution,

$$\begin{aligned} -\frac{\partial f_{ji}(\mathbf{r})}{\partial t} &= \text{div}_1 f_{ij}(-\mathbf{r}) \mathbf{v}_{ij}(-\mathbf{r}) + \text{div}_2 f_{ji}(\mathbf{r}) \mathbf{v}_{ji}(\mathbf{r}) \\ &= \text{div } f_{ji}(\mathbf{r}) [\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})] = 0 \end{aligned} \quad (15)$$

Here  $\mathbf{v}_{ji}(\mathbf{r})$  is the total velocity that the  $i$  ion has in the vicinity of a  $j$  ion and is given by

$$\mathbf{v}_{ji}(\mathbf{r}) = \omega_i \mathbf{k}_i - \omega_i kT \text{ grad}_2 \ln f_{ji}(\mathbf{r}) - \omega_i e_i \text{ grad}_2 \psi_i(\mathbf{0}) - \omega_i e_i \text{ grad}_2 \psi_j(\mathbf{r})$$

where  $\mathbf{k}_i$  is the applied force,  $\rho_i = 1/\omega_i$  the frictional coefficient,  $-\omega_i kT \text{ grad}_2 \ln f_{ji}(\mathbf{r})$  the diffusion velocity,  $-e_i \text{ grad}_2 \psi_i(\mathbf{0})$  the force due to the

<sup>24</sup> See references 22 and 25 for details.

ion's own atmosphere, and  $-e_j \text{grad}_2 \psi_j(\mathbf{r})$  the force due to the  $j$  ion and the latter's atmosphere. There is likewise a similar equation for  $\mathbf{v}_{ij}(-\mathbf{r})$ . If these equations for  $\mathbf{v}_{ij}(-\mathbf{r})$  and  $\mathbf{v}_{ji}(\mathbf{r})$  are substituted into equations 15, the following equations of motion are obtained,<sup>25</sup>

$$\begin{aligned} \text{div } f_{ji}(\mathbf{r})[\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})] &= \omega_i[\mathbf{k}_i \cdot \text{grad } f_{ji}(\mathbf{r})] - \omega_j[\mathbf{k}_j \cdot \text{grad } f_{ji}(\mathbf{r})] \\ &- n_j n_i [e_i \omega_i \Delta \psi_j(\mathbf{r}) + e_j \omega_j \Delta \psi_i(-\mathbf{r})] - kT(\omega_i + \omega_j) \Delta f_{ji}(\mathbf{r}) = 0 \end{aligned} \quad (16)$$

If, further, it is assumed that the external field is acting in the direction of the positive  $x$ -axis,  $\mathbf{k}_1 = X\mathbf{e}_1$ ,  $\mathbf{k}_2 = X\mathbf{e}_2$ , and bearing in mind that  $e_1 = -e_2 = e$  and  $n_1 = n_2 = n$ , the following equations are obtained from equation 16:

$$n^2 e \{ \Delta[\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r})] \} + 2kT \Delta f_{11}(\mathbf{r}) = 0 \quad (17)$$

$$-n^2 e \{ \Delta[\psi_2(\mathbf{r}) + \psi_2(-\mathbf{r})] \} + 2kT \Delta f_{22}(\mathbf{r}) = 0 \quad (18)$$

$$\begin{aligned} Xe(\omega_1 + \omega_2) \frac{\partial f_{12}(\mathbf{r})}{\partial x} - n^2 e \{ \omega_1 \Delta \psi_2(\mathbf{r}) - \omega_2 \Delta \psi_1(-\mathbf{r}) \} \\ + kT(\omega_1 + \omega_2) \Delta f_{12}(\mathbf{r}) = 0 \end{aligned} \quad (19)$$

$$\begin{aligned} -Xe(\omega_1 + \omega_2) \frac{\partial f_{21}(\mathbf{r})}{\partial x} - n^2 e \{ \omega_1 \Delta \psi_2(-\mathbf{r}) - \omega_2 \Delta \psi_1(\mathbf{r}) \} \\ + kT(\omega_2 + \omega_1) \Delta f_{21}(\mathbf{r}) = 0 \end{aligned} \quad (20)$$

As boundary conditions: For the flow, the vector field

$$f_{ji}(\mathbf{r})[\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})] \quad (21)$$

must be without sources. For the ionic fields, Wilson gives the following:

$$\left. \begin{aligned} \psi_1(\mathbf{r}) - e_1/Dr < \infty \\ \psi_2(\mathbf{r}) - e_2/Dr < \infty \end{aligned} \right\} \quad (22)$$

$$\psi_1(\infty) = \psi_2(\infty) = 0 \quad (23)$$

Equations 22 state that, since the space charge of the atmosphere is integrable, the potential  $\psi_j(\mathbf{r})$  at the point  $\mathbf{r}$  will differ from  $e_j/Dr$  only by a finite amount.

The Poisson equations may be expanded into the forms

$$\Delta \psi_1(\mathbf{r}) = \frac{4\pi e}{nD} [-f_{11}(\mathbf{r}) + f_{12}(\mathbf{r})] \quad (24)$$

<sup>25</sup> The expansion is accomplished by noting that the  $\mathbf{k}$ 's are divergence-free and that the following simplifications have been made. The  $\text{grad } \psi(0)$  terms have been neglected and the  $f_{ji}$  terms in the  $\text{grad } \psi(\mathbf{r})$  terms have been replaced by  $n_j n_i$ , since  $f_{ji} - n_i n_j \sim e_i e_j$ . Both of these simplifications are permissible because the terms neglected are of the order  $e_j^2$ , while the other terms are of the order  $e_j$ .



$$\Delta\psi_2(\mathbf{r}) = \frac{4\pi e}{nD} [-f_{21}(\mathbf{r}) + f_{22}(\mathbf{r})] \quad (25)$$

with similar equations with  $(-\mathbf{r})$ . In order to obtain one of the two symmetry relations for the potential, one Poisson equation is subtracted from another; this yields

$$\Delta[\psi_1(\mathbf{r}) - \psi_1(-\mathbf{r})] = \frac{4\pi e}{nD} [f_{12}(\mathbf{r}) - f_{12}(-\mathbf{r})] \quad (26)$$

$$\Delta[\psi_2(\mathbf{r}) - \psi_2(-\mathbf{r})] = \frac{4\pi e}{nD} [-f_{21}(\mathbf{r}) + f_{21}(-\mathbf{r})] \quad (27)$$

From equation 14 it is seen that

$$\Delta[\psi_2(\mathbf{r}) - \psi_2(-\mathbf{r}) - \psi_1(\mathbf{r}) + \psi_1(-\mathbf{r})] = 0$$

Since  $\psi_i(\infty) = \psi_i(-\infty) = 0$ , then

$$\psi_2(\mathbf{r}) - \psi_2(-\mathbf{r}) - \psi_1(\mathbf{r}) + \psi_1(-\mathbf{r}) = 0$$

or

$$\psi_2(\mathbf{r}) - \psi_2(-\mathbf{r}) = \psi_1(\mathbf{r}) - \psi_1(-\mathbf{r}) = 2Y(\mathbf{r}) \quad (28)$$

where  $Y(\mathbf{r})$  is the odd part of the potential, i.e., the part due to ions of unlike sign.

Since the boundary conditions for the flow stated that the vector field of the flow is without sources, the source-free vector vanishes so that

$$n^2 e [\psi_2(\mathbf{r}) + \psi_2(-\mathbf{r})] - 2kTf_{22}(\mathbf{r}) = \text{Constant}^{26}$$

Since  $f_{ii}(\infty) = n^2$ , the Constant =  $-2kTn^2$ . This gives, then,

$$f_{11}(\mathbf{r}) = f_{11}(-\mathbf{r}) = n^2 - \frac{n^2 e}{2kT} [\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r})] \quad (29)$$

$$f_{22}(\mathbf{r}) = f_{22}(-\mathbf{r}) = n^2 + \frac{n^2 e}{2kT} [\psi_2(\mathbf{r}) + \psi_2(-\mathbf{r})] \quad (30)$$

By means of the Poisson equations and these relations, the following equations are obtained:

$$(\Delta - \kappa^2/2)[\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r})] = \frac{4\pi e}{nD} [f_{12}(\mathbf{r}) + f_{12}(-\mathbf{r})]$$

$$(\Delta - \kappa^2/2)[\psi_2(\mathbf{r}) + \psi_2(-\mathbf{r})] = -\frac{4\pi e}{nD} [f_{21}(\mathbf{r}) + f_{21}(-\mathbf{r})]$$

<sup>26</sup> Found by writing equation 21 in its expanded forms.

These equations obviously lead to

$$(\Delta - \kappa^2/2)[\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r}) + \psi_2(\mathbf{r}) + \psi_2(-\mathbf{r})] = 0 \quad (31)$$

From the boundary condition (22) it follows that

$$\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r}) + \psi_2(\mathbf{r}) + \psi_2(-\mathbf{r}) < \infty$$

As Wilson pointed out, equation 31 has no solution other than zero, which is everywhere finite and free from singularities; thus

$$\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r}) + \psi_2(\mathbf{r}) + \psi_2(-\mathbf{r}) = 0$$

or

$$\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r}) = -[\psi_2(\mathbf{r}) + \psi_2(-\mathbf{r})] = 2\Gamma(\mathbf{r}) \quad (32)$$

where  $\Gamma(\mathbf{r})$  is the even part of the potential. From equations 28 and 32

$$\psi_1(\mathbf{r}) = -\psi_2(-\mathbf{r}) = \Gamma(\mathbf{r}) + Y(\mathbf{r}) \quad (33)$$

$$\psi_1(-\mathbf{r}) = -\psi_2(\mathbf{r}) = \Gamma(\mathbf{r}) - Y(\mathbf{r}) \quad (34)$$

*These equations describe the correct symmetry conditions of the ionic field for a binary electrolyte.<sup>27</sup>*

Denoting the even and odd parts of the function  $f_{12}(\mathbf{r})$  by  $G(\mathbf{r})$  and  $U(\mathbf{r})$ , we have

$$f_{12}(\mathbf{r}) = f_{21}(-\mathbf{r}) = G(\mathbf{r}) + U(\mathbf{r}) \quad (35)$$

$$f_{12}(-\mathbf{r}) = f_{21}(\mathbf{r}) = G(\mathbf{r}) - U(\mathbf{r}) \quad (36)$$

Using these relations and relations 33 and 34, equations 19 and 20 reduce to

$$\frac{n^2 e}{kT} \Delta \Gamma(\mathbf{r}) - \Delta G(\mathbf{r}) = \frac{eX}{kT} \frac{\partial U(\mathbf{r})}{\partial x} \quad (37)$$

$$\frac{n^2 e}{kT} \Delta Y(\mathbf{r}) - \Delta U(\mathbf{r}) = \frac{eX}{kT} \frac{\partial G(\mathbf{r})}{\partial x} \quad (38)$$

<sup>27</sup> Joos and Blumentritt in their work assumed that the perturbation of the distribution function,  $f'$  (where  $f = f^\circ + f'$ ) is small compared with  $f^\circ$ . This assumption is permissible only for low fields, where Ohm's law is valid, and leads to

$$\psi_1(\mathbf{r}) + \psi_1(-\mathbf{r}) = 0$$

and

$$\psi_1(\mathbf{r}) - \psi_1(-\mathbf{r}) = 0$$

Blumentritt, by assuming that these expressions are valid at high fields, has limited her results in this way. Consequently her theory gives only the correct sign and trend of the potential effect.

Introducing the symmetry conditions 33 and 34 into 29 and 30, we obtain

$$f_{11}(\mathbf{r}) = f_{22}(\mathbf{r}) = n^2 - \frac{n^2 e}{kT} \Gamma(\mathbf{r}) \tag{39}$$

When equations 33, 34, 39, 35, and 36 are combined with 24 and 25, we have

$$(\Delta - \kappa^2/2)\Gamma(\mathbf{r}) = \frac{4\pi e}{nD} G(\mathbf{r}) \tag{40}$$

$$\Delta Y(\mathbf{r}) = \frac{4\pi e}{nD} U(\mathbf{r}) \tag{41}$$

From equations 38 and 41,

$$(\Delta - \kappa^2/2)U(\mathbf{r}) = -\frac{eX}{kT} \frac{\partial G(\mathbf{r})}{\partial x} \tag{42}$$

and from equations 37 and 40

$$(\Delta - \kappa^2/2)G(\mathbf{r}) - \frac{\kappa^2}{2} \frac{n^2 e}{kT} \Gamma(\mathbf{r}) = -\frac{eX}{kT} \frac{\partial U(\mathbf{r})}{\partial x} \tag{43}$$

By applying the operator  $(\Delta - \kappa^2/2)$  to equation 38 and comparing with equation 42, we finally obtain

$$\Delta(\Delta - \kappa^2)G(\mathbf{r}) = \left(\frac{eX}{kT}\right)^2 \frac{\partial^2 G(\mathbf{r})}{\partial x^2} \tag{44}$$

Thus we have an equation in  $G(\mathbf{r})$  alone. Once this  $G(\mathbf{r})$  is known, we can obtain  $U(\mathbf{r})$ ,  $\Gamma(\mathbf{r})$ , and  $Y(\mathbf{r})$  from the equations 43, 40, and 41.

With the boundary condition for the flow, equation 21 becomes

$$f_{12}(\mathbf{r})[\mathbf{v}_{12}(\mathbf{r}) - \mathbf{v}_{21}(-\mathbf{r})] = \mathbf{S}_1$$

$$f_{21}(\mathbf{r})[\mathbf{v}_{21}(\mathbf{r}) - \mathbf{v}_{12}(-\mathbf{r})] = \mathbf{S}_2$$

Expanding these and using equations 33, 34, 35, and 36, we obtain for the symmetrical and asymmetrical parts of the flow

$$\mathbf{S}_s = \frac{n^2 e}{kT} \text{grad } \Gamma(\mathbf{r}) - \text{grad } G(\mathbf{r}) - \frac{eX}{kT} \mathbf{e}_z U(\mathbf{r}) \tag{45}$$

$$\mathbf{S}_a = \frac{n^2 e}{kT} \text{grad } Y(\mathbf{r}) - \text{grad } U(\mathbf{r}) - \frac{eX}{kT} \mathbf{e}_z G(\mathbf{r}) \tag{46}$$

where  $\mathbf{S}_1 = \mathbf{S}_s + \mathbf{S}_{a'}$ ,  $\mathbf{S}_2 = \mathbf{S}_{s'} - \mathbf{S}_{a'}$ ,  $\mathbf{S}_{s'} = \mathbf{S}_s(\omega_1 + \omega_2)$ ,  $\mathbf{S}_{a'} = \mathbf{S}_a(\omega_1 + \omega_2)$ , and  $\mathbf{e}_z$  is a unit vector.

Equations 42, 43, 40, 41, 44, 45, 46, together with the ionic boundary conditions

$$\lim_{\Omega=0} \int_{\Omega(S)} \text{grad}_n \Gamma(\mathbf{r}) \, dS = -\frac{4\pi e}{D}$$

$$\lim_{\Omega=0} \int_{\Omega(S)} \text{grad}_n Y(\mathbf{r}) \, dS = 0$$

where  $\Omega$  is the volume enclosed by the surface  $S$ , constitute a system of differential equations. On solving these equations we obtain the desired distribution and potential.

Since the field is parallel to the  $x$ -axis, cylindrical coordinates  $(x, \rho, \theta)$  are more convenient to use because the angle variable  $\theta$  drops out. Then, by Fourier transforms, Wilson finally obtains

$$\begin{aligned} f_{12}(\pm \mathbf{r}) = f_{21}(\mp \mathbf{r}) &= \frac{2}{\pi} \frac{n^2 \eta e}{D} \left[ \int_0^\infty \frac{1}{\sqrt{\kappa^4 - 4\mu^2 \alpha^2}} \right. \\ &\quad \left. \{(\lambda_1^2 - \alpha^2) K_0(\lambda_1 \rho) - (\lambda_2^2 - \alpha^2) K_0(\lambda_2 \rho)\} \cos(\alpha x) \, d\alpha \right. \\ &\quad \left. \pm \int_0^\infty \frac{\mu \alpha}{\kappa^4 - 4\mu^2 \alpha^2} \left\{ (\lambda_1^2 - \alpha^2) K_0(\lambda_1 \rho) + (\lambda_2^2 - \alpha^2) K_0(\lambda_2 \rho) \right. \right. \\ &\quad \left. \left. - \frac{\kappa^2}{2} K_0(\lambda_3 \rho) \right\} \sin(\alpha x) \, d\alpha \right] \quad (47) \end{aligned}$$

$$\begin{aligned} \psi_{1,2}(\mathbf{r}) &= \frac{2}{\pi} \frac{e}{D} \left[ \int_0^\infty \frac{\kappa^2}{\kappa^4 - 4\mu^2 \alpha^2} \left\{ (\lambda_1^2 - \alpha^2) K_0(\lambda_1 \rho) + (\lambda_2^2 - \alpha^2) K_0(\lambda_2 \rho) \right. \right. \\ &\quad \left. \left. - \frac{4\mu^2 \alpha^2}{\kappa^2} K_0(\lambda_3 \rho) \right\} \cos(\alpha x) \, d\alpha \right. \\ &\quad \left. \pm \int_0^\infty \frac{\kappa^2 \mu \alpha}{\kappa^4 - 4\mu^2 \alpha^2} \{K_0(\lambda_1 \rho) + K_0(\lambda_2 \rho) - 2K_0(\lambda_3 \rho)\} \sin(\alpha x) \, d\alpha \right] \quad (48) \end{aligned}$$

where  $\eta = e/kT$ ,  $\mu = \eta X$ , and  $K_0(\lambda \rho)$  is a modified Bessel function of the second kind and zero order, and  $\lambda = \lambda(\alpha)$  are functions of  $\alpha$  alone.<sup>28</sup>

$$\begin{aligned} \lambda_1^2 &= \alpha^2 + \frac{\kappa^2}{2} \left( 1 + \sqrt{1 - \frac{4\mu^2 \alpha^2}{\kappa^4}} \right) \\ \lambda_2^2 &= \alpha^2 + \frac{\kappa^2}{2} \left( 1 - \sqrt{1 - \frac{4\mu^2 \alpha^2}{\kappa^4}} \right) \\ \lambda_3^2 &= \alpha^2 + \frac{\kappa^2}{2} \\ \lambda_4 &= \alpha \end{aligned}$$

These expressions will now be used in calculating the electrophoresis and the ionic field.

To obtain the electrophoretic effect,<sup>29</sup> the calculation is carried out by using the classical hydrodynamical equation of Stokes for the velocity of a body in a viscous medium,

$$\begin{aligned}\eta_0 \operatorname{curl} \operatorname{curl} \mathbf{v} &= -\operatorname{grad} p + \mathbf{F} \\ \operatorname{div} \mathbf{v} &= 0\end{aligned}\tag{49}$$

where  $\eta_0$  is the viscosity,  $\mathbf{v}$  the vector velocity,  $p$  the pressure, and  $\mathbf{F}$  the force density due to the action of the external field  $\mathbf{X}$  upon the ion atmosphere. The problem is to solve equation 49. With Poisson's equation,

$$F_x = -\frac{DX}{4\pi} \Delta\psi\tag{50}$$

To solve equation 49 we find a vector  $\mathbf{a}$ , continuous everywhere, together with its derivatives up to the third order, and satisfying the equation

$$\eta_0 \nabla^2(\nabla^2 \mathbf{a}) = \mathbf{F}\tag{51}$$

Then

$$\mathbf{v} = -\operatorname{grad} \operatorname{div} \mathbf{A} + \nabla \cdot \nabla \mathbf{A} = -\operatorname{curl} \operatorname{curl} \mathbf{a}\tag{52}$$

and

$$p = \nabla^2(\operatorname{div} \mathbf{A})\tag{53}$$

Using equation 48 in equation 50, together with the above equations, the velocity of the central ion in the direction of the field axis is

$$v_z(0, 0, \theta) = -\frac{X e \kappa}{6 \sqrt{2} \pi \eta_0} f(x)\tag{54}$$

where

$$\begin{aligned}f(x) = 1 + \frac{3}{4 \sqrt{2} x^3} \left\{ -x \sqrt{1+x^2} + \sqrt{2} x \right. \\ \left. - (1+2x^2) \tan^{-1} \sqrt{2} x + (1+2x^2) \tan^{-1} \frac{x}{\sqrt{1+x^2}} \right. \\ \left. + 2x^2 \sinh^{-1} x \right\}\tag{55}\end{aligned}$$

and  $x = \mu/\kappa$ . In figure 16a  $f(x)$  is shown plotted as a function of  $x$ .

This figure shows very clearly how the complicated expression,  $f(x)$ ,

<sup>29</sup> See reference 22 and footnote 19 for a discussion.

varies with  $x$ , and that  $\lim_{x=0} f(x) = \sqrt{2}$  and  $\lim_{x=\infty} f(x) = 1$ . Consequently, if we let  $X = 0$ , we obtain the result of Onsager (22), whereas, for  $X = \infty$ ,

$$v_x(0, 0, \theta) = -\frac{e\kappa X}{6\sqrt{2}\pi\eta_0}$$

i.e., the electrophoretic effect does not disappear at infinite field.

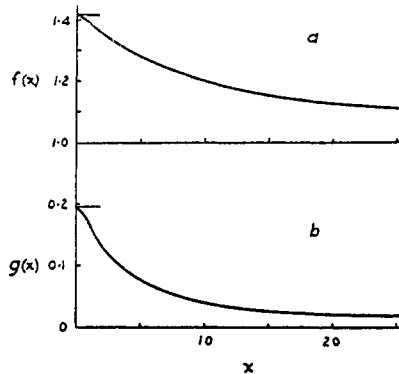


FIG. 16. The functions  $f(x)$  and  $g(x)$  plotted against  $x$

We obtain the added field acting on the ion in question due to the relaxation force,

$$\delta E(\mathbf{r}) = -\text{grad } \psi_i(\mathbf{r})$$

by using the  $\psi_i(\mathbf{r})$  from equation 48. This gives the ionic field at  $\mathbf{r}$ , and since we desire the field at the ion itself, we must evaluate the field at  $\mathbf{r} = 0$ ; i.e.,

$$\delta E(0) = \mathbf{e}_x \delta X(0, 0, \theta) = \lim_{x \rightarrow 0} \text{grad } \psi_i(x)$$

Performing the indicated operations we have

$$\delta X(0, 0, \theta) = \pm \frac{e\mu\kappa}{2D} g(x) \quad (56)$$

where

$$g(x) = -\frac{1}{2x^3} \left\{ -x\sqrt{1+x^2} + \tan^{-1} \frac{x}{\sqrt{1+x^2}} + \sqrt{2}x - \tan^{-1} \sqrt{2}x \right\} \quad (57)$$

Since  $g(x)$  is another complicated expression of  $x$ , it is most convenient to show graphically the variation of  $g(x)$  with  $x$ . This has been done

in figure 16b, from which it is apparent  $\lim_{x=0} g(x) = (2 - \sqrt{2})/3$  and  $\lim_{x=\infty} g(x) = 0$ . This simply means that for zero external field the expression 56 reduces to the required finite value and for infinite field the ionic field vanishes.

The final problem is to combine equations 54 and 56 in order to obtain the net velocity of the  $j$  ion in a field  $X$ .

$$v_j = X \left[ e_j \omega_j + \frac{\delta X_j(0)}{X} e_j \omega_j \right] + v_x(0, 0, \theta)$$

Here the first term on the right side is the velocity caused by the external and ionic fields, and  $v_x(0, 0, \theta)$  is that caused by the electrophoretic effect.

The mobility of the ion in practical units is

$$u_j = \frac{\omega_j}{300} = \frac{|v_j|}{300X}$$

and since the conductance for infinite dilution  $\Lambda_{\infty j} = 96500 u_{\infty j}$ , we have as the final equation

$$\Lambda_j = \Lambda_{\infty j} - \frac{|e_j|^2 \kappa}{2DkT} \Lambda_{\infty j} g(x) - (321.67) \frac{|e_j| \kappa}{6\sqrt{2} \pi \eta_0} f(x) \quad (58)$$

In order to show that this equation reduces to the quadratic form for very low fields, we expand the equation

$$\frac{\Delta\Lambda}{\Lambda_{E=0}} = \left( 1 - \frac{|e_j|^2 \kappa}{2DkT} g(x) \right) \frac{\Lambda_{\infty}}{\Lambda_{E=0}} - (643.34) \frac{|e_j| \kappa}{6\sqrt{2} \pi \eta_0} \frac{f(x)}{\Lambda_{E=0}} - 1 \quad (59)$$

for values of  $x^2 < 1$ . Neglecting terms of  $x^4$  and higher, we have<sup>30</sup>

$$\frac{\Delta\Lambda}{\Lambda_{E=0}} = \left[ (0.0344) \frac{|e_j|^2 \kappa}{2DkT} \frac{\Lambda_{\infty}}{\Lambda_{E=0}} + (0.0243)(643.34) \frac{|e_j| \kappa}{6\sqrt{2} \pi \eta_0} \frac{1}{\Lambda_{E=0}} \right] x^2 \quad (60)$$

We may quantitatively test the Wilson theory by means of Wien's data for magnesium sulfate (35, 36). The  $\Lambda_{E=0} - \sqrt{c}$  plot for magnesium sulfate is linear but does not have the theoretical slope, indicating a slight degree of incomplete dissociation. This manifests itself in such a way that in equation 59  $\lim_{x=0} \frac{\Delta\Lambda}{\Lambda_{E=0}} \neq 0$ . It is therefore necessary to add a constant to equation 59 which has such a value that for  $X = 0$  the curves pass through the origin. Equation 59, together with this constant, and equa-

<sup>30</sup> The Joos-Blumentritt theory gives for binary electrolytes 0.0133 instead of 0.0172 and 0.0973 instead of 0.0243.

tion 60 were used in the calculations. In figure 17 are shown the experimental points as well as the curves computed according to Wilson's theory. In this computation the constants used for the high-field region are  $c = 0.37 \times 10^{-3}$ ,  $\Lambda_{E=0} = 105.5$ ,  $\Lambda_{\infty} = 114$ ; and in the low-field region  $c = 1.22 \times 10^{-3}$ ,  $\Lambda_{E=0} = 99.0$ ,  $\Lambda_{\infty} = 114$ . In all the experimental work in Wien's laboratory the temperature was always about  $18^{\circ}\text{C}$ ., unless otherwise specified. In our calculations we therefore assumed  $D = 81$  and  $\eta_0 = 1.05 \times 10^{-2}$  c.g.s., corresponding to a temperature of  $18^{\circ}\text{C}$ . The deviations at high fields are due to the superimposition of the dissociation field effect, which is insignificant at the lower fields. Unfortunately, accurate data are not available for other electrolytes, and it is therefore impossible to say how generally a similarly good agreement will be found in the case of other electrolytes.

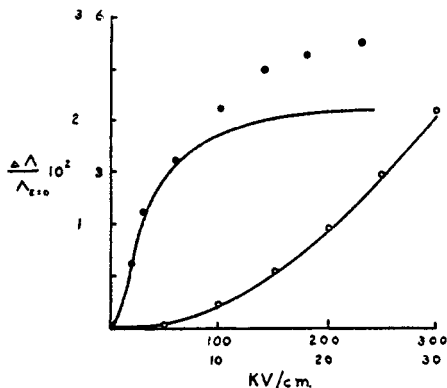


FIG. 17. Aqueous solutions of magnesium sulfate. ●, high field; ○, low field; —, theoretical curves

The theoretical equation (59) is extremely sensitive to the constants. It should therefore be emphasized that, in further studies in this field, accurate values be recorded for concentration, conductance corrected for solvent conductance, and temperature.

#### B. The theory of the dissociation field effect

In an attempt to account for the results obtained by Wien and his coworkers for weak electrolytes, Onsager (23) made a detailed study of the mechanism of association and dissociation of ions. He assumed that these processes are governed by the laws of Brownian motion. The distinction between free ions and ion pairs is the same as that of Bjerrum (2), who adopted the convention that two ions at a distance  $r < q$  are



considered as an ion pair. The potential of the average force between two such ions,  $i$  and  $j$ , is then

$$w_{ji}(r) = e_j e_i / Dr \quad \text{for } r < q \quad (61)$$

where  $q = e_j e_i / 2DkT$ . For  $r > q$ , this potential becomes

$$w_{ji}(r) = \frac{e_j e_i}{D} \frac{e^{(\kappa q - \kappa r)}}{(1 + \kappa q)r} \quad (62)$$

Onsager's considerations apply primarily to cases where the concentration of free ions is sufficiently small, so that

$$\kappa q = -\kappa e_1 e_2 / 2DkT \ll 1 \quad (63)$$

where

$$\kappa^2 = 4\pi(n_1 e_1^2 + n_2 e_2^2) / DkT \quad (64)$$

and  $n_1$  and  $n_2$  denote the concentration of free ions.

When no external field is present, the total concentration of ion pairs equals

$$\nu_{ji} = \nu_{ij} = n_i \int_a^q n_{ji}(r) 4\pi r^2 dr \quad (65)$$

where

$$n_{ji} = n_i e^{-w_{ji}/kT} \quad (66)$$

is the density of  $i$  ions in the neighborhood of  $j$  ions, and where  $a$  is the distance of closest approach of the two ions.<sup>31</sup> It is assumed that the ions are rigid spherical point charges, the sum of whose radii is  $a$ .

When an external electric field  $\mathbf{X}$  is applied, equation 66 is no longer valid. In the presence of such a field no true equilibrium exists between the ions and ion pairs, and it is accordingly necessary to consider the kinetics of dissociation and recombination of ions by applying the equations of Brownian motion (22, 25). The distribution function which results and which is considered to be applicable is the same as that given by equation 14. Again we have for the stationary condition,

$$\text{div}_2 [f_{ji}(\mathbf{r}) \{ \mathbf{v}_{ij}(-\mathbf{r}) - \mathbf{v}_{ji}(\mathbf{r}) \}] = 0 \quad (67)$$

where  $\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})$ , the mean relative velocity of the two ions at a distance  $\mathbf{r}$ , is given by

$$\begin{aligned} \mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r}) &= \omega_i [e_i \mathbf{X} + \mathbf{k}_{ji}(\mathbf{r}) - kT \text{grad}_2 \ln f_{ji}(\mathbf{r})] \\ &\quad - \omega_j [e_j \mathbf{X} + \mathbf{k}_{ij}(-\mathbf{r}) - kT \text{grad}_1 \ln f_{ij}(-\mathbf{r})] \end{aligned} \quad (68)$$

<sup>31</sup> For a critical discussion of ion pairs and their distribution function, see Fuoss (Trans. Faraday Soc. 30, 967 (1934)).

Here  $\mathbf{k}_{ji}(\mathbf{r})$  and  $\mathbf{k}_{ji}(-\mathbf{r})$  denote the average forces acting on the ion in question due to interactions with other ions. Assuming equation 63, the screening effect of the ion atmosphere is negligible so that

$$\begin{aligned}\mathbf{k}_{ji}(\mathbf{r}) &= -\text{grad}_2 w_{ji}(\mathbf{r}) \\ \mathbf{k}_{ji}(-\mathbf{r}) &= -\text{grad}_1 w_{ji}(\mathbf{r})\end{aligned}\quad (69)$$

where  $w_{ji}(r) = e_j e_i / Dr$ . Equations 68 and 69 lead to

$$\begin{aligned}f(\mathbf{r})\mathbf{v}(\mathbf{r}) &= f(\mathbf{r})[\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ji}(-\mathbf{r})] \\ &= kT(\omega_j + \omega_i) \left( -\text{grad} f + f \text{grad} \left( \frac{2q}{r} + 2\beta x \right) \right)\end{aligned}\quad (70)$$

where  $q = -e_1 e_2 / 2DkT > 0$  and

$$2\beta = |X(e_1 \omega_1 - e_2 \omega_2)| / kT(\omega_1 + \omega_2)$$

The frame of reference is such that the  $x$ -axis is parallel to the field  $\mathbf{X}$  and  $Xe_j > 0$  and  $Xe_i < 0$ . Therefore, equation 67 becomes

$$\text{div grad} f = \text{grad} f \cdot \text{grad} \left( 2\beta x + \frac{2q}{r} \right)\quad (71)$$

Furthermore, equation 70 with the equation of continuity yields the net rate of entry of pairs of ions into the interior ( $\Omega$ ) of any closed surface ( $S$ ) in the  $\mathbf{r}$  space, namely,

$$\int_{\Omega} \frac{\partial f}{\partial t} d\Omega = (\omega_j + \omega_i) kT \int_S \left[ \text{grad}_n f - f \text{grad}_n \left( \frac{2q}{r} + 2\beta x \right) \right] dS\quad (72)$$

where  $\text{grad}_n$  denotes the normal component of the gradient at  $S$ .

If Bjerrum's picture correctly describes the phenomenon of ion association, equation 71 must be solved with the boundary conditions

$$f = n_j n_i \quad (r = \infty)\quad (73)$$

and

$$f(\mathbf{r})\mathbf{v}(\mathbf{r}) = 0 \quad (r = a)$$

whence

$$\text{grad}_r f = f \left( 2\beta \cos \theta - \frac{2q}{r^2} \right) \quad \text{for } r = a\quad (74)$$

Since the boundary condition given by equation 74 is complicated, Onsager applied it under the simplifying assumption  $r = 0$ .

The solution of equation 71 is the subject of another paper by Onsager (24), but instead of solving this equation to satisfy both conditions 73 and 74, he proceeded to calculate separately the parts of  $f$  that correspond

individually to the processes of dissociation and recombination. To do this, he obtained the rate constants  $KA$  and  $A$  in the chemical kinetic equation

$$\frac{\partial \nu_{ji}}{\partial t} = A n_j n_i - KA \nu_{ji} \quad (75)$$

which is associated with the reversible reaction  $A^+, B^- \rightleftharpoons A^+ + B^-$ . The evaluation of these kinetic constants is equivalent to that of Langevin (15). Under the assumptions made, complete dissociation is represented by random distribution, i.e.,

$$f(\mathbf{r}) = n_j n_i \quad (76)$$

Accordingly, it follows from equations 72 and 76 that the rate of recombination is

$$A n_j n_i = 8\pi qkT(\omega_j + \omega_i)n_j n_i \quad (77)$$

whence for a binary electrolyte  $e_1 = -e_2$ ,

$$A = \frac{4\pi}{D}(e_1^2 \omega_1 + e_2^2 \omega_2) \quad (78)$$

It is now necessary to consider the case where the field  $X$  vanishes, in order to obtain that part of the distribution function which represents the associated ions. In connection with equation 62, Onsager points out that the factor  $e^{-\kappa r}$  is due to the gradual screening off of the electric field of an ion by the ion atmosphere and that neglect of this factor would lead to an infinite total space charge. Taking into account assumption 63, it is possible to neglect this factor up to some distance,  $r'$ , which fulfills the condition

$$a \ll r' \ll 1/\kappa \quad (79)$$

so that

$$w_{ji}(r) = e_j e_i / Dr \quad \text{for } r < r'$$

Now, according to condition 65, 76, and 79, the part of the distribution function representing the associated ions is

$$f(r) = n_j n_i (e^{2a/r} - 1) = \nu_{ji} K(0) (e^{2a/r} - 1) \quad (80)$$

This equation is the only solution of equation 71 that satisfies the following set of boundary conditions: (1)  $f = 0$  for  $r = \infty$ ; (2) there is a source of the given yield at the origin; and (3) the flow from the origin through any space angle is finite. Onsager states, however, that the solution of equation 71 for the field  $X \neq 0$  under these same boundary conditions

involves elaborate analysis, but that the unique result is expressed by the definite integral

$$f(r, \theta) = \frac{g}{r} e^{-\beta r + \beta r \cos \theta + 2q/r} \int_{s=0}^{s=2q} J_0[(-8\beta s)^{1/2} \cos \frac{1}{2}\theta] e^{-s/r} ds \quad (81)$$

where  $J_0[ ]$  denotes the ordinary Bessel function of order zero. If  $r$  is small, the upper limit<sup>32</sup> may be replaced by  $\infty$  to yield the result

$$f(r, \theta) \sim g e^{2qr} e^{2\beta r \cos \theta} \quad (82)$$

Onsager further reduces this expression by replacing  $e^{2\beta r \cos \theta}$  by unity, stating that the error introduced thereby may be of the same order of magnitude as that caused by neglecting the hydrodynamic interaction of the ions. Comparing the resulting simplified expression with equation 80, where  $e^{2q/r} \gg 1$ , it follows that

$$\nu_{ji} = g/K(0) \quad (83)$$

It is now necessary to evaluate the rate of dissociation by substituting the distribution 81 into the rate equation (72). If the integral in equation 81 is written  $\int_0^{2q} = \int_0^\infty - \int_{2q}^\infty$ , only the integral  $-\int_{2q}^\infty$  contributes to the flow, as Onsager points out, so that for small  $r$ ,

$$-K(X)A\nu_{ji} = -8\pi qkT(\omega_i + \omega_i)g \frac{J_1(4\sqrt{-\beta q})}{2\sqrt{-\beta q}}$$

Using equations 78 and 84, this reduces to

$$\frac{K(X)}{K(0)} = \frac{J_1(4\sqrt{-\beta q})}{2\sqrt{-\beta q}} = F(b) \quad (84)$$

Here

$$F(b) = 1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{1800} + \frac{b^5}{2700} + \frac{b^6}{56700} + \dots \quad (85)$$

for small values of  $b$ , or

$$F(b) \sim \sqrt{\frac{2}{\pi}} \frac{e^{(8b)^{1/2}}}{(8b)^{-3/4}} \left[ 1 - \frac{3}{8(8b)^{1/2}} - \frac{15}{128(8b)} - \frac{105}{1024[(8b)^{1/2}]^3} - \dots \right] \quad (86)$$

for large values of  $b$ . Equation 84 gives the increase of the dissociation constant due to the field, where the parameter  $b$  is

$$b = 2\beta q = \frac{z_1\omega_1 + z_2\omega_2}{\omega_1 + \omega_2} z_1 z_2 \frac{|X|e^3}{2Dk^2T^2}$$

<sup>32</sup> The error thus caused is negligible if

$$e^{\frac{2q}{r} - 4(\beta q)^{1/2}} \gg 1$$

Before proceeding further, it may be well to point out that equation 84 is an approximation which results on (1) assuming  $a = 0$  for the boundary condition (74), and (2) obtaining equation 82 by replacing the upper limit in equation 81 by  $\infty$  and setting  $e^{2\beta r \cos \theta} = 1$  in equation 82.<sup>33</sup> It may also be noted that the earlier equation (71) itself expresses the result of a simplified picture: (1) The hydrodynamic interaction of the ions is neglected, which may cause important errors in any solvent if the field is very high. (2) The shielding of the Coulomb forces due to the ion atmosphere has been neglected.

Physically, equation 84 states that while the dissociation of ion pairs is increased by the field, the recombination of ions remains unaffected (see equation 77). Considering the case of binary electrolytes, it is seen that

$$\frac{c\alpha^2}{1-\alpha} = K = K_0 F(b) \quad (87)$$

For small values of  $b$ , a good approximation is

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta\alpha}{\alpha_0} = \left( \frac{1-\alpha}{2-\alpha_0} \right) \frac{\Delta K}{K_0} = \frac{1-\alpha}{2-\alpha_0} b \quad (88)$$

where the increase of conductance  $\lambda$  is assumed proportional to the displacement of the dissociation equilibrium.

When the ions have the same charges, and the total number of ions is small compared to that of ion pairs, i.e.,  $\alpha \ll 1$ , then

$$\frac{\lambda}{\lambda_{g=0}} = \frac{\alpha}{\alpha_0} = \sqrt{\frac{K}{K_0}} = \sqrt{F(b)} = 1 + \frac{1}{2}b + \frac{1}{24}b^2 + \dots \quad (89)$$

It is of interest to point out that according to equation 89 the concentration of the electrolyte and the dimensions of the ions, as well as the equilibrium constant, have no influence on the value of  $\lambda/\lambda_{g=0}$ . In other words, for a given field this ratio depends only upon the charges on the ions, their mobility, the dielectric constant of the medium, and the temperature. Considering the case of a 1:1 salt under the action of the

<sup>33</sup> See footnote 32. If equation 71 is assumed valid for all distances,  $r = a$ , and if

$$\frac{q^2}{a^2(1-a\sqrt{\beta/q})} e^{-2q(1-a\sqrt{\beta/q})^2/a}$$

is small, the boundary condition for small  $r$  is immaterial. Since the errors caused by these simplifying assumptions are governed by values of  $\beta$  and  $q$ , we must consider the limits of these quantities. Since the intensities of the electrical field do not exceed 500 kilovolts per centimeter,  $\beta$  is limited to  $0 < \beta < 10^7 \text{ cm.}^{-1}$ . However, since  $q$  depends on the valence type of the electrolyte and on the dielectric constant of the solvent, considerable error may appear in equation 84 in solvents of high dielectric constant like water and acetone.

extreme field of 500 kilovolts per centimeter at 25°C., the resulting value obtained is  $\lambda/\lambda_{E=0} = 1.37$  for water and 121 for benzene. This may account for the large effect observed by Gyemant.

Onsager compares the consequences of this theory with available experimental data by means of equations 87 and 89, and discusses the results at some length. In figure 18, reproduced from Onsager's paper, are shown curves based on the experimental values of Schiele (28) for acetic and chloroacetic acids in aqueous solution. As may be seen from the figure, there is excellent agreement between the theoretical curve as drawn and the experimental points, except at low fields where deviations appear. This discrepancy is due to various simplifications and assumptions introduced in the course of developing the theory.

Necessary data are lacking for solutions in solvents of quite low dielec-

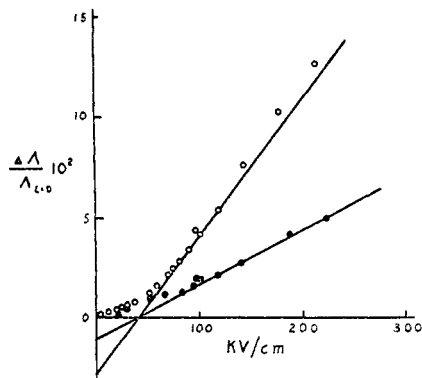


FIG. 18. ○, acetic acid; ●, chloroacetic acid; —, theory

tric constant. Fuoss and Mead<sup>34</sup> have measured the conductance of solutions of tetrabutylammonium picrate in diphenyl ether at 50°C. up to potentials of 20 kilovolts per centimeter. With a solution having a concentration of  $7.14 \times 10^{-3}$  moles per liter, they found that the conductance curve closely approximates the theoretical curve. They found, however, contrary to theory,<sup>35</sup> that the slope of the curve is a function of concentration and at other concentrations the variation amounts to as much as 40 per cent.

<sup>34</sup> These experiments have been carried out in the Research Laboratories of the General Electric Company and are as yet unpublished. We are indebted to Dr. R. M. Fuoss for this information.

<sup>35</sup> Onsager recently stated that perhaps by a more detailed analysis his theory could be extended to account for this concentration effect.

## IV. CONCLUSION

The deviations from Ohm's law for electrolytic solutions, discovered by Wien and exhaustively investigated by him and his coworkers, may be accounted for by the present theory of Coulombic interaction between the ions. The agreement between experiment and the theory of Wilson is remarkably good, considering the complexity of the hydrodynamical equations involved in the theoretical treatment and the difficulties encountered in the experimental determinations.

Although the present experimental material includes results covering most of the variable parameters involved, further studies of the dependence of the general Wien effect upon viscosity, dielectric constant, and temperature are greatly needed. The influence of frequency in the high-frequency ranges requires further and systematic investigation, particularly in view of the recent theory of Falkenhagen and Fleischer.

It is well established that, in solutions of weak electrolytes, the field effect is much larger than in solutions of strong (completely dissociated) electrolytes. The parallelism found between the field effect and the strength of the electrolyte leaves little room for doubt that the external field increases the number of free ions in the solution. Onsager's theory of the field effect in solutions of weak electrolytes accounts remarkably well for the observed experimental results in the few instances where the necessary data are available for making the comparison. Investigation of the field effect in solutions of incompletely dissociated electrolytes is much needed, particularly for solutions in solvents of low dielectric constant where the phenomenon is greatly simplified owing to the low concentration of free ions.

The investigation of the influence of the electric field on the properties of electrolytic solutions, theoretical as well as experimental, has served not only to disclose many new and interesting phenomena, but also to place the theory of these solutions on a thoroughly secure foundation. The ions as well as the products of their interaction have taken on a degree of physical reality, the lack of which previously made it so difficult for many chemists to accept the ionic theory.

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