

APPLICATION OF THE FERMI STATISTICS TO THE
DISTRIBUTION OF ELECTRONS UNDER FIELDS IN
METALS AND THE THEORY OF
ELECTROCAPILLARITY¹

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ABSTRACT

It is assumed that each atom in mercury is ionized into a positive ion and an electron. Because of the crowded state of the positive ions it is supposed that they cannot move in an electric field, while, following Sommerfeld and Pauli, the electrons are assumed to act like a completely degenerate gas following the Fermi statistics. The distribution of electrons under an electric field due to a charge on the surface of the metal is discussed, and a relation derived which gives the charge on the surface in terms of the potential difference between surface and interior. To a first approximation the charge and potential difference are proportional to each other, as if there were a condenser of constant capacity at the surface. In order to find the capacity an estimate must be made of the dielectric constant of the mercurous ions of the mercury. This is done with the aid of measurements of the refractive index of mercurous ions. The magnitude of the equivalent capacity is such that, when considered in conjunction with the diffuse layer of ions in the solution, electrocapillary curves can be explained.

INTRODUCTION

THE distribution of solute ions under the electric field caused by a charge on the surface of the solution was first investigated by Chapman.³ He used these considerations in an attempt to explain the shape of the electrocapillary curve in the region of its maximum, assuming that the mercury was a perfect conductor so that the charge resided on its surface, while the ions formed a diffuse atmospheric layer in the solution. But, as shown by Frumkin,⁴ Chapman's theory did not explain the experimental facts.

Recently the present writer⁵ applied Chapman's equations for the distribution of ions to the ions and electrons in mercury, and by assuming that there was a diffuse layer on both sides of the solution-mercury boundary showed that a fair, but still not perfect agreement between electrocapillary measurements and theory could be obtained. These considerations assumed that mercury ions and electrons formed perfect solutes in the mercury, and involved the use of Boltzmann's law for the distribution of ions in the electric field, that is the density of ions (or electrons) at any place in the field was put proportional to $e^{-U/kT}$, U being the energy of an ion (or electron) at a

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³ Chapman, *Phil. Mag.* (6) **25**, 475 (1913).

⁴ Frumkin, *Phil. Mag.* (6) **40**, 384 (1920).

⁵ Rice, *J. Phys. Chem.* **30**, 1501 (1926).

given place due to the potential of the field, k Boltzmann's constant, and T the absolute temperature. Since it was found that, in order to fit the electrocapillary data, we had to assume that only a small proportion of the mercury atoms were ionized into mercury ions and electrons the assumption of Boltzmann's law appeared to be justified at the time. Indeed, it was to be supposed that it would hold for the electrons to fairly high concentrations, and this fact, it may be stated, would have precluded any attempt to account for the experimental facts by supposing that all the mercury atoms were ionized, but that due to the crowded condition of the positive ions Boltzmann's law could not hold for them.

The writer also showed that the facts could about equally well be accounted for by another theory. In this case it was assumed that the mercury was a perfect conductor, but that between the mercury and the solution there was a condenser of constant capacity, due perhaps to the ions not being able to approach clear to the surface.⁶ In the solution itself there was assumed to be the usual diffuse atmospheric layer of ions.

Since the publication of this paper a new proposal has been made in the theory of metals. Pauli⁷ and Sommerfeld⁸ applied the Fermi⁹ statistics to "electron gas" in metals and found that it would be completely degenerate at ordinary temperatures. The latter showed that, on the basis of this theory, contact potentials between metals are given by the equation

$$\phi_2 - \phi_1 = \frac{h^2}{2m\epsilon} \left\{ \left(\frac{3n_2}{4\pi} \right)^{2/3} - \left(\frac{3n_1}{4\pi} \right)^{2/3} \right\} \quad (1)$$

where h is Planck's constant, m the mass and ϵ the charge on an electron, n_1 the number of free electrons per unit volume in the first metal and n_2 in the second, and ϕ_1 and ϕ_2 the potentials of the two metals. By setting n_1 and n_2 equal to the number of atoms per unit volume of the respective metals he obtained contact potentials of the right order of magnitude, though of the wrong sign.¹⁰ On the whole, his considerations seem to indicate that, while the theory may not be entirely correct in detail, its general features have much to recommend them. So we will now reconsider the case of two diffuse layers, using this theory for the diffuse layer in mercury, and the usual one for the aqueous diffuse layer.

DISTRIBUTION OF ELECTRONS AT THE CHARGED SURFACE OF THE METAL

In the case of electrocapillarity, the electric field in the mercury is produced by an excess of ions of one sign in the solution, which is always balanced by an excess or deficiency of electrons near the surface of the mercury.

⁶ Stern, *Zeits. f. Elektrochem.* **30**, 508 (1924).

⁷ Pauli, *Zeits. f. Physik* **41**, 81 (1927).

⁸ Sommerfeld, *Naturwissenschaften* **15**, 826 (1927).

⁹ Fermi, *Zeits. f. Physik* **36**, 902 (1926).

¹⁰ Sommerfeld did not take into account the difference of the "thermodynamic environment" of the electrons in the two metals. We deal with a single metal.

We will let the excess of positive electricity per unit surface on the solution side of the boundary be Q_0 ; this is the surface charge for all considerations concerned with the mercury side of the boundary. The potential at the surface of the mercury above that of its interior we shall call ϕ_0 ; it will have the same sign as Q_0 . From our considerations of the distribution of the electrons we shall find Q_0 in terms of ϕ_0 . The corresponding relation for the aqueous side of the boundary is known, and the surface tension can be found in the manner described in our previous work.

Near the surface of the mercury, as noted above, there will be an excess or deficiency of electrons, and Eq. (1) must hold for the potential difference between two points near the surface in the same metal, as well as for the potential difference between the interiors of different metals. From it follows immediately

$$d\phi = A dn_x^{2/3} \quad (2)$$

where ϕ is the potential (the potential far from the surface being taken as zero) and n_x the density of electrons at a given point, and

$$A = [h^2/(2m\epsilon)] \times [3/(4\pi)]^{2/3} = 1.93 \times 10^{-17} \quad (3)$$

Now we shall assume that each mercury atom gives just one electron. The electrons, being small and freely moving except for the restrictions of the quantum mechanics as shown by Fermi's calculations, will distribute themselves according to Eq. (2). The mercury ions, however, are large and closely packed, and as a first approximation we may assume that their density is the same at the surface as in the interior of the metal. This mass of ions will have a dielectric constant, which we shall designate as K . The density of the ions, which is the same as the density of electrons far in the body of the metal, we shall denote by n_∞ . The density of electricity at any point will be given by

$$\rho = \epsilon(n_\infty - n_x) \quad (4)$$

According to Poisson's equation we have

$$\nabla^2\phi = -4\pi\rho/K$$

which reduces in our case (assuming a flat surface, since, as we shall see, the radius of curvature in any practical case will be great compared to the thickness of the surface layer) to

$$d^2\phi/dx^2 = 4\pi\epsilon(n_x - n_\infty)/K. \quad (5)$$

From Eq. (2), $A d^2 n_x^{2/3}/dx^2 = d^2\phi/dx^2$.

Combining with Eq. (5), $A d^2 n_x^{2/3}/dx^2 = 4\pi\epsilon(n_x - n_\infty)/K$

By multiplying through by $2dn_x^{2/3}/dx$ this equation can be put in the form

$$A \frac{d(dn_x^{2/3}/dx)^2}{dx} = \frac{16\pi\epsilon}{5K} \frac{dn_x^{5/3}}{dx} - \frac{8\pi\epsilon n_\infty}{K} \frac{dn_x^{2/3}}{dx}$$

Integrating from the surface ($x=0$) to $x=\infty$, remembering that at $x=\infty$ we have $dn_x^{2/3}/dx=0$ and $n_x=n_\infty$, and designating quantities at the surface by a subscript zero, we get

$$-A\left(\frac{dn_x^{2/3}}{dx}\right)_0^2 = \frac{16\pi\epsilon}{5K}(n_\infty^{5/3} - n_0^{5/3}) - \frac{8\pi\epsilon n_\infty}{K}(n_\infty^{2/3} - n_0^{2/3}) \quad (6)$$

Now $n_0^{2/3} - n_\infty^{2/3} = \phi_0/A$ or $n_0^{2/3} = n_\infty^{2/3} + \phi_0/A$. Raising both sides of this equation to the 5/2 power we get (since, as we shall see, $n_\infty^{2/3} > |\phi_0/A|$)

$$n_0^{5/3} = n_\infty^{5/3} + (5/2)n_\infty(\phi_0/A) + (15/8)n_\infty^{1/3}(\phi_0/A)^2 + (5/16)n_\infty^{-1/3}(\phi_0/A)^3 + \dots$$

Also $(dn_x^{2/3}/dx)_0 = (1/A)(d\phi/dx)_0 = -4\pi Q_0/(AK)$. So we see that Eq. (6) takes the form

$$Q_0^2 = \frac{3K\epsilon n_\infty^{1/3}\phi_0^2}{8\pi A} \left(1 + \frac{1}{6} \frac{\phi_0}{An_\infty^{2/3}} + \dots\right) \quad (7)$$

Now for mercury $n_\infty = 4.1 \times 10^{22}$ per cc so if ϕ_0 is of the order of 0.7 volts or 7/3000 e.s.u. as in the cases we shall discuss $\phi_0/(An_\infty^{2/3}) = 0.1$, so that for a first approximation we may neglect the terms after the first in Eq. (7). This means that to a first approximation the diffuse layer in the mercury acts like a condenser of constant capacity given by

$$Q_0/\phi_0 = (3K\epsilon/8\pi A)^{1/2} n_\infty^{1/6} \quad (8)$$

and this case reduces to the second one discussed in the introduction, that of a diffuse layer in the aqueous part and a condenser of constant capacity. If we can determine K we can compare the capacity of the condenser with the capacity which best fits the data as found in our previous work.

THE DETERMINATION OF K AND COMPARISON OF THE THEORETICAL AND OBSERVED CAPACITIES

The medium in which the electrons are dispersed may be considered to more or less resemble a mass of mercurous ions. Accordingly we shall determine K from the mole refraction¹¹ of mercurous ions. The mole refraction, R , is defined by the following equation

$$R = V(r^2 - 1)/(r^2 + 2) \quad (9)$$

where V is the volume occupied by one mole of the substance considered

¹¹ Pauling, Proc. Roy. Soc., A 114, 181 (1927). See especially Eq. (20) of Pauling's article. That the dielectric constant which we calculate is the right one can be seen as follows. If the ions and electrons were point charges in vacuum we would simply have a distribution of electrons and ions in a medium of dielectric constant 1. Actually, however, the ions are polarized in an electric field, and it does not matter whether the electric field is applied from within, as in this case, or from without, as in the case of light going through a crystal. The electrons do not contribute to the dielectric constant, since we are considering a definite distribution of them (i.e., the equilibrium distribution); they are taken account of explicitly in our equations, as is the net charge on the ions. Only the polarizability of the latter, which is the polarizability of mercurous ions, is included in the dielectric constant.

and r is its index of refraction. In a mixture of substances the mole refractions are additive. If the substance is non-magnetic

$$r^2 = K \quad (10)$$

According to Groth¹² the index of refraction of mercurous chloride varies in different directions from 1.95 to 2.60. We take 2.27 as a rough average. Hylleraas¹³ finds the density to be 7.21. We then calculate the mole refraction¹⁴ to be 19.00. According to Pauling¹⁵ the mole refraction for chloride ion in crystals lies between 8.04 and 8.48. Taking 8.26 as the approximate value we find the mole refraction of mercurous ions to be 19.00–8.26 or 10.74. From the known density of mercury we then calculate r^2 or K for the assumed mercurous ions in the metal to be 8.9. Using Eq (8) we find the capacity of the equivalent condenser to be 3.0×10^7 e.s.u., which is equivalent to a plate condenser in vacuum whose plates are of unit area and 2.65×10^{-9} cm apart. In our previous work we found that the condenser which best fits the data would have its plates at a distance of 2.3×10^{-9} cm apart, giving it a capacity of 3.5×10^7 e.s.u.

This quantitative correspondence leads one to believe that the existence of a condenser (for which the evidence is very strong¹⁶) is probably due to the distribution of electrons in the mercury rather than to other causes, such as the ions in the solution being unable to approach clear to the surface. It may be stated that if the presence of the condenser were due to the latter cause, and we supposed the medium surrounding the ions determined the dielectric constant of the condenser, we find from the dielectric constant of water that the actual distance between the plates of the condenser would have to be about 2×10^{-7} cm—much too large to be reasonable. This may not, however, be a conclusive argument against this supposition, since it is so hard to form a picture of the actual conditions at the surface. We may state, however, that if it is proper to apply Fermi statistics to electrons in metals that some phenomenon such as we have described must occur, and our object is to show that the idealized picture we have presented does give results which agree quantitatively with available data. The various possibilities have not, of course, been exhaustively considered.

In order to get further comparison with experimental data we may perhaps examine the region of the electrocapillary curve where the potential difference is somewhat greater than that considered in our previous paper. It is sometimes unsatisfactory to apply theoretical considerations to the high voltage region of the curve because of the tendency of ions to pile up

¹² Groth, "Chemische, Krystallographie," Wilhelm Engelmann (1906), v. I, p. 215. The values given are for the red lithium line but will not be very different for infinite wave-length.

¹³ Hylleraas, *Zeits. f. Physik* **36**, 861 (1926).

¹⁴ We have arbitrarily used the formula HgCl instead of Hg_2Cl_2 . This makes no difference in the final value of the dielectric constant.

¹⁵ Ref. 11, p. 196. We neglect any polarization of the ions with respect to other ions due to movement of the ions as a whole, simply subtracting the value for chloride ion given by Pauling from the value of the mole refraction of mercurous chloride.

¹⁶ At least the diffuse aqueous layer alone cannot explain the facts.

at the surface of the solution. However, according to the present theory, a large part of the potential drop takes place in the mercury. In fact, when the total potential drop between the solution and the mercury is 0.74 volts (fairly high for our considerations) there is only a voltage drop of 0.07 in a solution of 1 N uni-univalent electrolyte. In such a case the concentration of ions of one sign or the other becomes theoretically 16.4 N at the surface. When the total potential drop is 0.46 volts the concentration at the surface becomes 7.4 N. These concentrations are perhaps rather large, but at least the solution is not nearly filled with ions at such concentrations. Besides, most of the lowering of surface tension is due to the mercury side of the boundary where such disturbances do not occur (as may be seen from our previous estimate of $\phi_0/(An_\infty^{2/3})$ or $(n_0^{2/3} - n_\infty^{2/3})/n_\infty^{2/3}$); and the determination of the surface tension involves an integration with respect to potential, including therefore regions where these disturbances do not occur and so somewhat lowering their effect. It is, in fact, my belief, that the capacity of the equivalent condenser determined from the electrocapillary curve in this way is more accurate than that cited from our previous paper.

Krüger and Krumreich¹⁷ decided that of all substances KNO_3 showed the fewest anomalies in its electrocapillary curve. Such anomalies would invalidate the considerations of our previous article in which the calculation of the surface tension due to the combination of the condenser with the diffuse aqueous layer is considered, and since they have only to do with the aqueous side we wish naturally to avoid them for our present purposes. Krüger and Krumreich found with a 1 N solution of KNO_3 an almost perfectly parabolic electrocapillary curve, corresponding to a capacity of 27 microfarads, or 2.4×10^7 e.s.u. We have made calculations, as in our former paper, from 0.0 to 0.741 volts, assuming the equivalent condenser in the mercury to have a capacity as found above of 3.0×10^7 e.s.u. Since most of the potential drop takes place in this condenser we might expect the curve to be nearly parabolic, in spite of the aqueous layer, and it is, within limits of error. When the aqueous layer is included the equivalent capacity of the whole comes out to be 2.7×10^7 e.s.u. The agreement is about as good as we found before. The discrepancy is in the opposite direction. Altogether, the coincidence of the calculated and experimental values is remarkable.

NON-AQUEOUS SOLUTIONS, ETC.

Frumkin¹⁸ finds that for nitrates in methyl and ethyl alcohols and acetone the ascending branch of the curve is parabolic, indicating about the same capacity as in the case of water. This is what is expected, since we believe the electrocapillary curve to be chiefly determined by the mercury. But the descending branch is also parabolic with a shape corresponding to a lower capacity. It thus appears that the thickness of the condenser is greater on the descending than on the ascending branch. It may be that this is to be explained by the presence of an impenetrable monomolecular film of solvent

¹⁷ Krüger and Krumreich, *Zeits. f. Elektrochem.* **19**, 620 (1913).

¹⁸ Frumkin, *Zeits. f. Phys. Chem.* **103**, 43 (1922).

which occurs in the descending branch when the mercury is negatively charged, but not when it is positively charged. With aqueous solutions such a film would have to be rather thick to cause an appreciable effect because of the high dielectric constant of water; organic liquids, however, have much lower dielectric constants. Thus there is *a priori* more reason for such an effect to show up in the case of organic liquids than in the case of water. Furthermore, organic liquids wet mercury better than water,¹⁹ which probably means that such a film would be more easily formed. The existence of such a film is supported by Frumkin's data for lithium chloride in different strengths of alcohol.¹⁸ It seems to appear only when the mercury is negatively charged, which may be evidence in favor of the supposition that the more positive portions of the molecules of solvent are attracted to the surface.

Turning to an entirely different case, a curve obtained by von Hevesy and Lorenz²⁰ with molten lead and molten potassium chloride seems to show a much lower capacity than can be readily accounted for. But such curves have not been exhaustively studied and difficulties and peculiarities would be likely to arise. For example, the capillary electrometer is insensitive and depolarization is great.

Lastly, we may make a remark about the effect of temperature on the ordinary electrocapillary curves.²¹ It is small, as would be expected from the fact that Eq. (8), which chiefly determines the effect, according to our theory, has no temperature coefficient.

DISCUSSION

We may now consider some of the points which may be brought against our theory. In the first place, objection may be brought against the application of the Fermi statistics in metals, as being either essentially incorrect or too great an idealization. These questions unfortunately become confused when experimental tests are being made. The use of the Fermi statistics is of course tentative, but, as stated above, there seems to be reason to believe that, for certain purposes at any rate, it can serve as a good approximation. Attempts to develop the theory on more exact lines are likely to lead to complications which will sooner or later necessitate approximations as severe.

We should, of course, take into account the effect of the positive ions on the electrons, but at present it seems probable that at least one electron per atom is comparatively free.⁸ If it were necessary to take into account un-ionized atoms, it might be possible for charged positive ions to replace uncharged ones, thus leading to complications.

In our calculations we assumed that the electrons were free to move through the whole space occupied by the mercury. It might be that only a fraction of the space, say f , could be occupied by the electrons. If now n_x and n_∞ retain their meanings as numbers per *total* volume Eq. (4) would remain

¹⁹ Harkins in Bogue's "Colloidal Behavior," McGraw-Hill Book Co. (1924), v. I, p. 177.

²⁰ von Hevesy and Lorenz, *Zeits. f. Phys. Chem.* **74**, 454 (1910).

²¹ Vining, *Ann. Chim. Phys.*, (8) **9**, 281 (1906).

unchanged since the ρ to be used in Poisson's equation is the amount of electricity per unit total volume. But we should have to replace Eq. (2) by $d\phi = Adn_x^{2/3}/f^{2/3}$. On carrying through the calculations the right hand side of Eq. (8) would be multiplied by $f^{1/3}$, i.e. it would result in the calculated capacity being decreased by a factor $f^{1/3}$, but the effect would not be expected to be important.

Had we made the assumption that each mercury atom was ionized into two electrons and a doubly charged ion our calculations would have been unchanged, but we should have to substitute double the value for n_∞ and an appropriate value of K in Eq. (8). The formula is very insensitive to changes in n_∞ since it appears to the $1/6$ power. If, however, we use the value, 3.14, given by Pauling²² for the mole refraction of mercuric ions, we get a considerably different value for K , and the distance of the plates of the equivalent condenser in vacuum turns out to be 5.2×10^{-9} . This causes us to favor the assumption that there is only one free electron per mercury atom.²³

Another objection centers around the application of statistical methods to an effect which takes place so near the surface. Actually a layer of molecular thickness is involved.²⁴ Against this objection may be urged the fact that we wish to consider average conditions at the surface, and that the surface contains many molecules. The method is not an unusual one. We have, of course, neglected surface perturbations, which might be important in so thin a layer. Final decision in these matters must perhaps wait, but the agreement with the electrocapillary experiments is evidence in favor of our method.

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²² Ref. 11, p. 195.

²³ The note added in proof makes the choice less definite.

²⁴ The calculation is made as follows. Eq. (8) will hold not only for the surface, but for any point a distance x from the surface. If Q_x includes all the charge between the point x and the surface added algebraically to the charge on the aqueous side of the surface, then

$$Q_x/\phi_x = (3K\epsilon/8\pi A)^{1/2} n_\infty^{1/6}$$

But $Q_x = -(K/4\pi)(d\phi/dx)_x$. So, substituting this value of Q_x , integrating from 0 to x , and taking the exponential of each side we get

$$\phi_x/\phi_0 = \exp \left[-(6\pi\epsilon/K A)^{1/2} n_\infty^{1/6} x \right]$$

The exponent is -1 if x is 2.4×10^{-8} cm, which means that all but a fraction $1/e$ of the potential drop occurs in this distance from the surface. On the aqueous side of the boundary the drop of potential will usually occur in a similar distance.

Note added in proof, April 25, 1928—Since this paper was submitted for publication a more detailed account of the new electron theory has appeared in papers by Sommerfeld and others (*Zeits. f. Physik* **47**, 1, 33, 38, 43 (1928)). In these articles a correction is made which results in a slight change in our Eq. (1), which now becomes

$$\phi_2 - \phi_1 = \frac{h^2}{2m\epsilon} \left\{ \left(\frac{3n_2}{4\pi G} \right)^{2/3} - \left(\frac{3n_1}{4\pi G} \right)^{2/3} \right\}$$

where G is a weight factor that is given the value 2 to allow for the two spin quantum numbers of the electron. This would cause the right hand side of Eq. (8) to be multiplied by $2^{1/3}$, causing the calculated capacity of the condenser in the mercury to become 3.8×10^7 e.s.u. instead of 3.0×10^7 and the equivalent capacity when the aqueous layer is included to become about 3.25×10^7 instead of 2.7×10^7 . This change is in the opposite direction to that which would be produced by correcting for the part of the metal the electrons cannot occupy.