The Nature of Adsorbed Films of Caesium on Tungsten. Part I.
The Space Charge Sheath and the Image Force

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State of thermal equilibrium in an enclosure having tungsten walls and containing caesium vapor.—In a large heated enclosure having tungsten walls and containing Cs vapor in thermal equilibrium, there are ions, electrons and atoms, with concentrations given by $n_e n_p/n_a = K$ where the equilibrium constant K can be calculated from the ionizing potential of Cs vapor. The interior of the enclosure constitutes a typical *plasma* with $n_e = n_p$. Near the walls are *space charge sheaths* in which particles of only one sign are usually present. The potential distribution of the weak fields that reach into the plasma are governed by the Debye-Hückel theory characterized by the Debye distance λ_D. The sheaths contain an excess (or deficiency) of ions and there is a corresponding sheath adsorption which is related to a negative surface tension (spreading force F) by Gibbs' adsorption equation.

Electrc image forces near plane metallic surfaces.—Still closer to the surface there is an *image force sheath* in which the distribution of ions and electrons is governed mainly by the image force $f = (e/2x)^2$. Throughout both the space charge and the image sheaths, the concentration of electrons or ions (whichever is larger) is given by $n = \exp(x_s/x)/8\pi x_s(x+x_L)^2$ where x_s, the *Schottky distance*, is $e^2/4kT$ and x_L is the *v. Laue distance* equal to $(kT/2\pi e^2 n_1)^{\frac{1}{2}}$, n_1 being the concentration at the boundary between the space charge sheath and the image sheath (corresponding to the saturation current).

Perturbation method for the study of image forces.—Within distances of a few Angstroms from the surface, the classical image force requires modification because the "effective reflecting plane" which determines the location of the image, changes its position as any given electron or ion approaches the surface. The image force for ions is thus greater than for electrons when these particles are at a given distance from the surface. A general method is devised for calculating the image force (a second approximation) acting on electrons very close to the surface. An approximate calculation of the electron distribution is made and then the *perturbations* produced by a given electron are used to determine the image force on that electron. In a modification of this method, the perturbation produced by a given electron in the distribution of neighboring electrons is considered to be characterized by a *perturbation free path* which is used to calculate the location of the reflecting plane and the resultant image force.

Application of methods to electrons with Fermi distribution.—These methods are used to calculate the image force on a given electron resulting from electrons near the surface of a metal (both inside and outside of it) which have a Fermi distribution consistent with the Poisson equation. A third approximation can then be made by considering that all of the electrons in the *Fermi sheath* are similarly acted on by an image force so that the sheath becomes much thinner than calculated by the second approximation. In Part II of this paper it will be shown that, because of the thinness of this sheath, it becomes possible to calculate the image force far more accurately by a new *displacement method* than by these two approximations. Similar image force considerations should govern all applications of the Fermi theory to concentrated electron atmospheres in which there are large concentration gradients.

WHEN caesium vapor, saturated at room temperature (about 0.001 barye) comes into contact with a hot tungsten filament, an adsorbed film of caesium is formed on the filament. The properties of such films have been quite extensively studied.[1-8] Methods have been devised for measuring ν_a, ν_p and ν_e (the rates of evaporation of atoms, positive ions and electrons) as functions of the temperature T and of σ, the number of adsorbed atoms per unit area.

Schottky[9] derived theoretically the following relation between the energies of evaporation of

[1] I. Langmuir and K. H. Kingdon, Science 57, 58 (1923), and Phys. Rev. 21, 380 (1923).

[2] H. E. Ives, Phys. Rev. 21, 385 (1923); Astrophys. J. 60, 209 (1924).

[3] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. A107, 61–79 (1925).

[4] J. A. Becker, Phys. Rev. 28, 341–61 (1926).

[5] J. A. Becker, Trans. Am. Electrochem. Soc. 55, 153 (1929).

[6] I. Langmuir, J. Am. Chem. Soc. 54, 1252 (1932).

[7] I. Langmuir and J. B. Taylor, Phys. Rev. 40, 463 (1932).

[8] I. Langmuir, J. Am. Chem. Soc. 54, 2798 (1932). See especially pp. 2816–2831.

[9] W. Schottky, Ann. d. Physik 62, 142–55 (1920).

atoms, ions and electrons and the ionizing potential of the atoms

$$U_a + U_i = U_p + U_e. \tag{1}$$

All these quantities are conveniently expressed in equivalent electron-volts, so that U_i is then the ionizing potential.

Langmuir and Kingdon[1] found experimentally that ν_p and ν_a are dependent on the electron affinity U_e of an adsorbed surface film of Cs on tungsten, and thus depend on ν_e. They concluded that the stability of the adsorbed film "is due to the fact that the electron affinity of a tungsten surface ($U_e = 4.62$ volts) is greater than that of caesium ions (ionizing potential $U_i = 3.88$ volts)."

A little later, M. v. Laue[10] showed theoretically that the concentrations of atoms, electrons and ions in equilibrium with a heated metal cannot be independent of one another, but must be so related as to give the proper degree of ionization for the vapor in accord with Saha's equation.[11]

The ease and accuracy with which the properties of caesium films may be determined experimentally renders them particularly suitable for fundamental investigations of the electrical properties of adsorbed films and of the forces acting between atoms on the surfaces of metals.

In an analysis[6, 8] of the experimental data of Dr. J. Bradshaw Taylor on the atom evaporation rate ν_a, a theory has been developed by which the forces between the adsorbed atoms (adatoms) can be calculated from the variation of ν_a with σ. This theory was based on the concept that the adsorbed film acts like a two-dimensional gas whose spreading force F (dynes cm^{-1}) is related on the one hand to ν_a by Gibbs' equation for the adsorption isotherm, and on the other hand to $f(r)$, the law of force between adatoms, by the Clausius virial equation. The results indicated that the adatoms behave as dipoles of moment M oriented with their axes normal to the surface, the positive end facing outward. The force of repulsion between adatoms at a distance r is thus $f = (3/2)M^2r^{-4}$. The moment M varies with the surface concentration σ because of the depolarizing force produced by neighboring adatoms.

[10] M. v. Laue, Sitzb. Preuss. Akad. Wiss. 32, 334–48 (1923).

[11] M. N. Saha, Zeits. f. Physik 6, 40 (1921), and Phil. Mag. 44, 1128 (1922).

From these values of M, by means of the Boltzmann and the Saha equations, values of ν_e and ν_p as functions of T and σ were obtained and were found to agree well with those given by the experiments.

Although this agreement may be regarded as justification of the use of the Gibbs and Clausius equations in the treatment of this problem, there are several theoretical questions that need more careful analysis. For example, the adsorbed film of caesium was assumed to be a monatomic film with all the adatoms in one plane. This raises the question as to the distribution of atoms, ions and electrons in the space near the metal surface. Are the adsorbed atoms all on the surface or do they constitute a miniature atmosphere extending some distance from the surface?

Since the distribution of electrons within the metal and close to its surface follows the Fermi rather than the classical distribution law, any accurate calculation of the forces acting between the adatoms and the underlying metal is a difficult problem in quantum mechanics. At distances from the surface only slightly greater than atomic dimensions, the laws of quantum mechanics rapidly approach those of the classical theories.

The object of the present paper is to analyze the conditions of equilibrium between electrons, ions and atoms of an alkali metal vapor in an enclosure bounded by metallic walls. At large distances from the walls the conditions resemble those of the Debye-Hückel theory of electrolytes. Then there is a region where space charge is the dominant factor. Still nearer the metallic surface the distribution is governed by the image force. Extremely close to the surface space charge again becomes important, but in this region the quantum rather than the classical laws are applicable.

By this procedure of deriving knowledge of conditions near the surface from our more certain knowledge of the regions far from the surface, we shall avoid many of the difficulties that would be involved in an attempt to treat the surface conditions directly.

I. State of Thermal Equilibrium in an Enclosure

Consider an enclosure containing alkali metal vapor in thermal equilibrium at the temperature

T. Let n_e, n_p, n_a be respectively the average number of electrons, positive ions and atoms per unit volume at any given point within the enclosure.

Electrical pressure resulting from segregation

At sufficiently high concentrations of ions and electrons the electrical forces between the particles must cause deviations from the ideal gas laws. Debye and Hückel[12] have developed the theory of such forces for electrolytic solutions and their equations are applicable to ionized gases. The effect of the charges on the ions and electrons is to cause each ion to be surrounded by an increased concentration of electrons (and *vice versa*), so that the lines of force emanating from the ion do not extend to infinity but terminate within a finite distance. We shall refer to this phenomena as segregation.[13] The potential in the neighborhood of an ion, instead of falling off in proportion to $1/r$, varies in proportion to $(1/r)$ exp $(-r/\lambda)$, where the constant λ may be called the *Debye distance*. Its value, calculated by Debye and Hückel by simultaneous solution of the Boltzmann and Poisson equations, is

$$\lambda = (kT/4\pi e^2(n_e+n_p))^{1/2}$$
$$= 4.896 \ (2T/(n_e+n_p))^{1/2} \text{ cm}, \quad (2)$$

where k is the Boltzmann constant 1.371×10^{-16} erg deg.$^{-1}$ and e is the electronic charge 4.770×10^{-10} e.s.u. according to Birge.[14]

The total pressure p exerted by the ionized gas is then

$$p = nkT - e^2(n_e+n_p)/6(\lambda+a), \quad (3)$$

where $n = n_a+n_e+n_p$, and a is the effective distance of nearest approach of the ions and electrons, or, by combining with Eq. (2) and neglecting a compared to λ,

$$p = nkT - 5.476\times10^{-21}(n_e+n_p)^{3/2}T^{-1/2} \text{ barye.} \quad (4)$$

The first term in the right-hand member of Eq. (3) corresponds to the ideal gas law while the second term represents what may be called the *electric pressure*. As n_e+n_p increases, the

total pressure rises at first in proportion to n, but then more slowly until at a certain value $(n_e+n_p)_M$ the pressure reaches a maximum value p_M. We then have

$$(n_e+n_p)_M = 4(kT)^3/\pi e^6 = 2.786\times10^8 T^3 \text{ cm}^{-3}. \quad (5)$$

By analogy with van der Waal's theory of the transition from the gaseous to liquid states, we may conclude that just before n_e+n_p reaches the value $(n_e+n_p)_M$, the electric forces should make the gas phase unstable so that a *condensed phase* should appear in which there is a far higher concentration than given by $(n_e+n_p)_M$. From Eq. (5) we see, however, that with temperatures of the order of 1000°K such instability would occur only when the concentration of ions and electrons becomes about 3×10^{17} cm^{-3}, while for all concentrations below about 10^{15} the effect of the electric pressure may be neglected.

Very close to a metal surface, because of the electric image force, the concentrations of ions and electrons may reach values as great as 10^{17}, so that from the foregoing considerations we might expect a condensed phase to appear. We shall see, however, that other factors make this improbable unless negative ions are also present.

Equilibrium constants

At concentrations so low that the electric pressure is negligible, the law of mass action gives

$$K_n = n_e n_p/n_a, \quad (6)$$

where K_n, the equilibrium constant for any given vapor, is a function only of temperature. The value of K_n as a function of temperature is found[15] to be

$$K_n = (\omega_e\omega_p/\omega_a)[(2\pi m_e kT)/h^3]$$
$$\times \exp(-U_{i0}e/kT), \quad (7)$$

where U_{i0} is the ionizing potential of the alkali atom at the absolute zero and the ω's are the statistical weights of the normal states of the free electrons, ions and atoms. For the vapors of the alkali metals these have the values $\omega_e = \omega_a = 2$ and $\omega_p = 1$. Inserting Birge's numerical values[14] for m_e, k and h, and expressing the concentration in terms of cm^{-3}, we obtain

$$K_n = 2.447\times10^{15}T^{3/2} \exp(-11606U_i/T), \quad (8)$$

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[12] P. Debye and E. Hückel, Phys. Zeits. **24**, 185–206 (1923), and P. Debye, ibid. **25**, 97–107 (1924); see also A. A. Noyes, J. Am. Chem. Soc. **46**, 1080–97 (1924).

[13] See a paper entitled *Forces near the Surfaces of Molecules*, I. Langmuir, Chem. Rev. **6**, 451–79 (1929), especially pp. 459–60.

[14] R. T. Birge, Rev. Mod. Phys. **1**, 1 (1929).

[15] R. H. Fowler, *Statistical Mechanics* (1929), p. 281.

where U_i is measured in volts. For convenient calculation this may be written,

$$\log_{10} K_n = 15.3886$$
$$+ (3/2) \log_{10} T - 5040 U_{i0}/T. \quad (9)$$

The ionizing potentials of the alkali metals can be accurately calculated from the $1S$ terms in the spectrum. Taking the wave numbers given for these terms by Franck and Jordan[16] and dividing by 8106 as given by Birge,[14] we obtain the following values of U_{i0} expressed in volts: Cs, 3.874; Rb, 4.155; K, 4.318; Na, 5.113 and Li, 5.364.

There are several other possible definitions of the equilibrium constant.[17] One in very common use is

$$K_p = p_e p_p / p_a \quad (10)$$

where p_e, p_p and p_a are the partial pressures of electrons, ions and atoms. Since $p = nkT$,

$$K_p = kT K_n. \quad (11)$$

In experiments with tungsten filaments in alkali metal vapors, we do not measure n or p directly, but determine the rate at which atoms, ions or electrons strike the filament surface or evaporate from it. Let μ_e, μ_p and μ_a be the number of electrons, ions or atoms per unit time per unit area that cross any given imaginary surface in the gas. Classical kinetic theory then gives

$$\mu = p(2\pi mkT)^{-1/2} = n(kT/2\pi m)^{1/2}. \quad (12)$$

For electrons[14] $m_e = 9.035 \times 10^{-28}$g, so that

$$\mu_e = 1.554 \times 10^5 n_e T^{1/2}, \quad (13)$$

while for ions of molecular weight M (O atom $= 16$), $m_p = 1.649 \times 10^{-24} M$ gram, giving

$$\mu_p = 3637 n_p (T/M)^{1/2}. \quad (14)$$

This may also be used for calculating μ_a.

In terms of the pressure p_a (in baryes)

$$\mu_a = 2.653 \times 10^{19} p_a (MT)^{-1/2}. \quad (15)$$

The rates of flow of electrons and ions to any

[16] J. Franck and P. Jordan, Handb. d. Physik, Berlin 23, 703 (1926).

[17] Much of the nomenclature used in the present paper and some of the methods of reducing non-equilibrium conditions to equilibrium were introduced in connection with a study of the dissociation of hydrogen into atoms, I. Langmuir, J. Am. Chem. Soc. 38, 1145–56 (1916).

metallic electrode are directly measurable as current. The current density I in amperes cm^{-2} is thus

$$I = e\mu = 1.591 \times 10^{-19} \mu. \quad (16)$$

Even the rate of flow of alkali metal atoms, μ_a, can be measured as a current I_a by heating a filament to such high temperature that all atoms which strike it are converted to ions. We thus have two other useful equilibrium constants:

$$K_\mu = \mu_e \mu_p / \mu_a \quad \text{and} \quad K_I = I_e I_p / I_a. \quad (17)$$

The relations between these "constants" are

$$K_\mu = (kT/2\pi m_e)^{1/2} K_n = 1.554 \times 10^5 T^{1/2} K_n, \quad (18)$$

$$K_I = eK_\mu = 2.472 \times 10^{-14} T^{1/2} K_n \text{ amp. cm}^{-2}. \quad (19)$$

Potential distribution

Since the relative numbers of electrons and ions emitted by the walls of the enclosure depend on the material of the walls, n_e and n_p are not always equal and therefore there will be a space charge $\rho = e(n_p - n_e)$.

The potential distribution is related to ρ in accordance with Poisson's equation $\Delta V = -4\pi\rho$.

In a state of thermal equilibrium and at concentrations so low that the electrical pressure is negligible, the distribution of ions and electrons is given by the Boltzmann equations,

$$n_e = n_0 \epsilon^\eta, \qquad n_p = n_0 \epsilon^{-\eta}, \quad (20)$$

where η is a dimensionless parameter proportional to V defined by

$$\eta = Ve/kT = 11600 V/T \quad (21)$$

if V is measured in volts. The zero of potential is taken to be that which makes $n_e = n_p = n_0$.

The value of n_0 is readily obtained from Eq. (6) by placing $n_e = n_p = n_0$ so that

$$n_0^2 = n_a K_n. \quad (22)$$

If with any given value of n_0 the enclosure is made of sufficiently large size, n_e and n_p will be practically equal throughout the enclosure except near the walls. If we neglect, for the present, forces acting on the ions or electrons due to the charges they induce individually on the walls (image force), we find that the potential distri-

bution near any plane bounding surface is given[18] by

$$x = \lambda_0 \ln (\tanh (\eta_1/4)/\tanh (\eta/4)) \qquad (23)$$

where λ_0 is the Debye distance obtained from Eq. (2) by putting $n_e = n_p = n_0$, and x is the distance from the wall to any point whose potential is V. The value of η_1 is found by substituting $V = V_1$ in Eq. (21), V_1 being the potential at the wall $(x = 0)$.

Expansion of Eq. (23) gives

$$x/\lambda_0 = \ln \tanh (|\eta_1|/4) - \ln (|\eta|/4)$$
$$+ (1/48)\eta^2 - (7/23040)\eta^4 + \cdots . \qquad (24)$$

In all the cases that are of interest to us $|\eta_1| \gg 1$. For small values of η, that is, when $\eta^2 < 1$, we may neglect the first term of the second member of Eq. (24) so that the equation reduces to

$$|\eta| = 4\epsilon^{-x/\lambda_0}. \qquad (25)$$

The potential thus falls to $1/\epsilon$th value for each increment of x equal to the Debye distance λ_0. The potential and the concentrations become uniform at a distance from the wall which is a small multiple of λ_0.

When $\eta^2 \gg 1$, Eq. (20) shows that there are particles of only one sign present.

We see that there are two rather distinct regions to be considered. In the interior of the enclosure where $\eta^2 < 1$, and n_e is approximately equal to n_p, we have a typical *plasma*[19] in which there are only weak fields and the logarithm of the potential varies linearly with distance in accord with Eq. (25). Close to the walls where $\eta^2 > 1$ are typical *sheaths* where there are strong space charges due to charged particles which are all of the same sign. These sheaths, however, differ from those near collectors in gaseous discharges in that here, under the equilibrium conditions that prevail, there are present the trapped electrons (or ions) necessary to give the complete Maxwell-Boltzmann distribution. This produces

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[18] Equations equivalent to Eq. (23) have been derived for electrolytic solutions by K. F. Herzfeld, Phys. Zeits. **21**, 28 (1920), and for ionized metal vapors by M. v. Laue, Preuss. Akad. Wiss. Berlin, Ber. **32**, 334–48 (1923), see p. 340; Handb. d. Radiologie **VI**, 472–8 (1925); R. H. Fowler's *Statistical Mechanics*, Cambridge Univ. Press (1929), p. 283.

[19] I. Langmuir, Phys. Rev. **33**, 954–89 (1929). See particularly pp. 964, 979, 980.

an extremely rapid change in potential very close to the walls.

Potential and concentration in the space charge sheath

Since within the sheath particles of one sign predominate, we may conveniently omit the subscripts p and e in designating the concentration and use n to represent the concentration of the particles which are present in excess while n' is used for the particles present only as a minority. Thus by Eq. (20) we have

$$n = n_0 \exp (|\eta|), \quad n' = n_0 \exp (-|\eta|) \qquad (26)$$

and

$$nn' = n_e n_p = n_0^2. \qquad (27)$$

We may let n_1 be the value of n at the surface of the electrode, i.e., at $x = 0$. The value of n_1 depends on the electron emission or the positive ion emission (whichever is larger) from the metal surface, in accord with Eqs. (13) or (14).

Eq. (23) may now be put in a more convenient form by substituting a new variable defined by

$$u = \exp (-|\eta|/2) = (n_0/n)^{1/2}. \qquad (28)$$

We thus obtain for $u < 1$

$$\ln \tanh (\eta/4)$$
$$= \ln \frac{1-u}{1+u} = -2\left(u + \frac{u^3}{3} + \frac{u^5}{5} + \cdots \right). \qquad (29)$$

If $(1/3)u^2$ can be neglected compared to unity, each member of Eq. (29) equals $-2u$ and thus Eq. (23) reduces to

$$x + x_L = 2\lambda_0 u = 2\lambda_0 (n_0/n)^{1/2}, \qquad (30)$$

where x_L is a parameter having the dimensions of a length, which we may call the *v. Laue distance*. Its value is

$$x_L = 2\lambda_0 u_1 = 2\lambda_0 (n_0/n_1)^{1/2}. \qquad (31)$$

If we introduce the value of λ_0 as given by Eq. (2) these equations may be written

$$x + x_L = (kT/2\pi e^2 n)^{1/2} = 9.792(T/n)^{1/2} \text{ cm}, \qquad (32)$$

$$x_L = (kT/2\pi e^2 n_1)^{1/2} = 9.792(T/n_1)^{1/2} \text{ cm}. \qquad (33)$$

These equations give the distribution of the concentration n within the space charge sheath. The concentration n' of the minority particles is readily calculated by Eq. (27) from n_0 as given

by Eq. (22). The potential distribution is given by Eq. (26). The 3d column of Table I gives the values of x_L for a series of values of n_1.

Within the *plasma* the potential distribution is given by Eq. (25) while within the *sheath* it may be obtained from Eq. (32). Although the boundary between these two regions is of course not sharp, there is a narrow region in which both Eqs. (25) and (32) are approximately fulfilled. Thus if we place $|\eta| = 1.5$ (or $V = \pm 1.3 \times 10^{-4}T$ volts) we find that Eq. (25) gives $x = 0.98\lambda_0$, and Eqs. (30) and (28) give $x = 0.945\lambda_0$, while the rigorous Eq. (23) gives $x = 1.026\lambda_0$.

Sheath adsorption

If the radius of curvature for all parts of the surface of the enclosure is large compared to λ_0, we may look upon the ionized gas as constituting a field-free and electrically neutral plasma except within plane sheaths covering the walls. These sheaths have many properties which may profitably be considered as belonging to the metal surface which they cover. For example, the excess or deficiency of ions integrated throughout the thickness of the sheath is a part of the total adsorption by the metal surface. There is also a surface free energy or negative surface tension associated with the sheath which, in thermodynamical calculations, is to be included in the spreading force F of the adsorbed film on the surface. For such purposes, of course, the effects due to the fields extending into the plasma for distances several times λ_0 should be included with those in the sheath proper.

Let σ_s be the total amount per unit area of *adsorbed* material in the form of positive ions within the sheath, so that

$$\sigma_s = \int_0^\infty (n_p - n_0)dx.$$

Inserting the value of n_p from Eq. (20) and expressing dx in terms of η by differentiating Eq. (23) we obtain

$$\sigma_s = 2n_0\lambda_0(\epsilon^{-\eta_1/2} - 1). \quad (34)$$

If we replace η_1 in this equation by η, σ_s becomes the total amount adsorbed per unit area in that part of the sheath which lies between the plasma and the plane at which the potential cor-

responds to η. Eliminating η by means of Eq. (20) and inserting the value of λ_0 from Eq. (2) we get

$$\sigma_s = (kT/2\pi e^2)^{1/2}(n_p^{1/2} - n_0^{1/2}). \quad (35)$$

If the potentials in the sheath are positive, $n_p < n_0$ and there is, according to Eq. (34), a negative adsorption in the sheath which cannot exceed $2n_0\lambda_0$. With negative sheath potentials, however, the positive ion adsorption is positive and rapidly becomes equal to $4n_0\lambda_0^2/x_L$. In this case it can be shown by Eqs. (34), (28), (30) and (31) that half of the total amount adsorbed within the sheath lies within the distance x_L of the surface.

Surface tension in the sheath

M. v. Laue[20] has calculated the surface tension resulting from an electron sheath on the surface of a hot metal. For this purpose he adds the total energy of the electrostatic field per unit area to the total force per unit length exerted by the electron atmosphere on a plane perpendicular to the sheath. These two effects contribute equally to the resulting surface tension.

Carrying through a similar calculation for the sheaths produced with ionized metal vapor that we are now considering, we obtain rigorously

$$U_s = [(kT)^{3/2}/e(2\pi)^{1/2}][n_p^{1/4} - n_e^{1/4}]^2 \quad (36)$$

or

$$U_s = 1.342$$
$$\times 10^{-15}T^{3/2}(n_p^{1/4} - n_e^{1/4})^2 \text{ erg·cm}^{-2}, \quad (37)$$

where U_s is the total electrostatic energy per sq. cm between the interior of the plasma and the plane at which the ions and electrons have the concentrations n_p and n_e. Since the *pressure* of the electrons and ions (in excess over that in the plasma) contributes an equal part, the surface spreading force is

$$F = 2U_s. \quad (38)$$

If $n_e \gg n_p$, the value of F is the same as that given by the equation derived by v. Laue.

Comparison of F and σ_s by Gibbs' equation for adsorption

The general statement of Gibbs' law for the

[20] Max v. Laue, Jahr. d. Radioakt. 15, 238 (1918).

adsorption isotherm[21] is

$$dF/d \ln a = \sigma kT, \tag{39}$$

where F is the spreading force, a is the activity of the adsorbed vapor in the gaseous phase in equilibrium with the solid, and σ is the number of atoms adsorbed per unit area. The derivative $dF/d \ln a$ represents the rate of change of F when $\ln a$ is changed by altering the concentration in the gas phase while the surface area of the adsorbing surface is kept constant.

This equation should be applicable to the values of F and σ_s which we have obtained in Eqs. (35), (36) and (38). Let us eliminate n_p by Eq. (20) and thus obtain

$$F = 2kTB(n_0^{1/2} - n_e^{1/2})^2, \tag{40}$$

$$\sigma_s = B[n_0 - (n_e n_0)^{1/2}], \tag{41}$$

where

$$B = (kT/2\pi e^2 n_e)^{1/2} = 9.792 T^{1/2} n_e^{-1/2}. \tag{42}$$

In these equations n_e represents the electron concentration at the metal surface, or rather at a distance from the surface at which the image force is negligible.

Let us now consider a case in which n_e is determined by the electron emission characteristic of the material of the walls unaffected by the presence of adsorbed films which might alter the contact potential. This condition can readily be realized at high temperatures, and particularly with metals having high electron emissivity which have little tendency to adsorb ions.

Eq. (39) can be written

$$\ln a = \int dF/\sigma_s kT. \tag{43}$$

Inserting the values of F and σ_s and integrating, taking n_e to be constant, we obtain for all values of n_0

$$a = \text{const.} \times n_0^2 = \text{const.} \times n_a. \tag{44}$$

Thus we see that the values of F and σ_s are consistent with Gibbs' equation. The activity a is proportional to the concentration n_a of atoms. This result is in accord with the ordinary use of Gibbs' equation. Since in all practical cases n_0 is negligibly small compared to n_a, the degree of

[21] Thermodynamics by Lewis and Randall, McGraw-Hill (1923), pp. 250 and 251.

ionization in the plasma is not enough to influence the activity a. In Langmuir and Kingdon's[3] previous use of the Gibbs' equation, they erroneously took the activity to be proportional to n_p and were thus led to draw the incorrect conclusion that under certain conditions caesium adatoms attracted one another.

II. Conditions at Plane Metallic Surfaces. Electric Image Forces

The essential characteristic of metallic conductivity is that no steady electrostatic field can be maintained within the conductor except by the continual expenditure of energy. Under equilibrium conditions the surface of any metal must be an equipotential surface. If an electric field E exists outside the metal so that lines of force reach the metal surface, the direction of the field at the surface must be normal to the surface, and since these lines must terminate at the surface, there must be a surface charge s given by $E = -4\pi s$.

Potential distribution

The potential distribution in a region containing space charges near a plane conducting surface is ordinarily calculated by Poisson's equation

$$d^2 V/dx^2 = -4\pi\rho \tag{45}$$

together with the boundary condition $V = $ constant over the conducting surface. The electric force acting on any electron is then $e\,dV/dx$ (or $-e\,dV/dx$) for a positive ion of charge $+e$.

This method, which considers a continuous distribution of charge, is strictly justifiable only if the effects due to the discrete nature of the electric charges are negligible.

The obvious need, under certain conditions, for modifications in the theory to take into account the actual discontinuous distribution, has led to frequent confusion, to numerous errors and to much discussion. It seems worth while, therefore, to examine rather critically the nature of the forces acting on electrons or ions which are close to ideal metallic surfaces (equipotential surfaces).

In free space the potential at distance r from a point charge e is e/r; but if this point charge lies at a position A close to a semi-infinite mass of metal bounded by an equipotential plane sur-

face S, the potential at any point P outside the metal is equal to $(e/r) - (e/r')$. Here r is the distance from P to A', where A' is the electric image of A in the surface, A and A' being symmetrically located with respect to S. Thus with any number of charged particles the potential at P is

$$V = \Sigma(e/r) - \Sigma(e/r'). \tag{46}$$

A term corresponding to the image potential is absolutely necessary in order that S may be an equipotential surface. It is, however, equally possible to write the equation in the form

$$V = \Sigma(e/r) + \int ds/r_s, \tag{47}$$

where s represents the surface charge density at any point on the surface whose distance from P is r_s. The integration is to be carried over the whole surface S.

Since the charged particles to be considered are moving rapidly (velocities negligible compared to light), it is obvious that the potential V at any point will fluctuate with time. The value of V given by Eq. (46) is thus to be regarded as an instantaneous value corresponding to any given instantaneous positions of the particles. We can use such values of V to calculate the instantaneous force which the *potential field* would exert on a small charge placed at the position P, but must be careful not to use these fluctuating values of V to calculate changes in the energies of a charged particle at different times. For example, in general it will not be true that $\Delta Ve = \Delta(\frac{1}{2}mv^2)$.

This use of Eq. (46) theoretically gives a complete general solution for the potential distribution and should be used whenever the detailed effects of the discontinuous distribution are to be taken into account. However, we ordinarily do not know the instantaneous positions of all the charged particles: we know only certain average values of the concentrations. The problem of greatest present interest to us is to determine how the concentration n of electrons or ions varies close to a metallic surface. We need then to adopt a suitable definition of n.

Jeans[22] discusses the relative merits of several

definitions for the density of a gas. If the distribution of matter were continuous, the density would normally be defined as the limiting value of m/v, the ratio of mass to volume, as v shrinks to infinitesimal size. But with a discontinuous distribution the limit of m/v is zero for all elements of volume except those containing a particle, and is infinite for the latter.

With an infinite quantity of a homogeneous gas consisting of molecules, the density could be defined as the limiting value of m/v as v is increased indefinitely.

For gases which are neither continuous nor homogeneous, Jeans finds it impossible to choose a rigorous definition but adopts as a practical one the ratio m/v in which v is taken of such size that it "may, without appreciable error, be supposed to be infinitely great in comparison with the distance between neighboring molecules, and at the same time infinitely small compared with the scale of variation of density of the gas." Very close to a metal surface we shall see that the density may vary enormously within distances far less than the average distance between neighboring molecules, so that Jeans' definition of density becomes meaningless.

We are, however, interested primarily in systems in equilibrium which are not assumed to be undergoing any progressive change with time. The difficulties of Jeans' definitions are thus completely avoided if we adopt Fowler's[23] suggestion that *time averages* instead of space averages be used. Thus if v is a small volume enclosing the point P, and N is the number of electrons within v at any given time t, we may define n as the limiting value of $[\int_0^t (N/v)dt]/t$ as we let t approach infinity and then make v infinitesimally small.

The probability that a particle will occur at any instant of time within dv is thus $n\,dv$. As an alternative definition of n we may say that n is the *probability per unit volume* for the occurrence of an electron at P. We see then that n varies continuously throughout space, although at each instant the distribution of charge is discontinuous.

Similarly in dealing with other properties which characterize assemblies of electrons and

[22] J. H. Jeans, *Dynamical Theory of Gases*, Cambridge, 2nd Edition (1916), p. 14.

[23] R. H. Fowler, *Statistical Mechanics*, Cambridge (1929), p. 8.

ions in equilibrium, we should deal with time averages. Thus in the Boltzmann equation[24] $n = n_0 \epsilon^{Ve/kT}$, both n and V are time averages and are not instantaneous values or local values.

We have seen that Eq. (46) enables us to calculate the instantaneous potential V for any given distribution of charged particles near a surface. If, however, we use this equation to find the time average potential $\bar{V}$ in a series of successive intervals, it becomes

$$V = \int ne \, dv/r - \int ne \, dv/r' \qquad (48)$$

where the first integral extends through the space outside the metal, while the second covers the corresponding hypothetical space on the other side of S.

This equation is, however, exactly equivalent[25] to Poisson's equation with $\rho = ne$, and with the boundary condition $\bar{V} = 0$ at the surface S.

Therefore we are justified in using the Poisson equation alone, instead of Eq. (46) or (47), whenever we wish to know merely the average potential $\bar{V}$.

There is thus no need to take into account the discrete nature of the charged particles in calculating the potential distribution for use in connection with the Boltzmann equation. This is *true even though the average distance between the charged particles is large compared to the distance of the particles from the surface of the metal.*[26]

We shall have occasion to consider the discontinuous distribution of space charge in determining the conditions under which the ideal gas laws may be applied to concentrated space charges very close to metal surfaces.[27]

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[24] R. H. Fowler, *Statistical Mechanics* (1929), see pp. 48 and 188.

[25] See Handb. d. Physik **12**, 375 (1927).

[26] R. S. Bartlett in a recent paper, Phys. Rev. **37**, 959–69 (1931), especially on pages 958 and 969, questions the validity of Poisson's equation when used in this way. He seems to think that Poisson's equation is applicable accurately only when the distance between neighboring electrons, $n^{-1/3}$ (?) is small compared to x, the distance to the surface S. Failure to distinguish between instantaneous and average values of V has probably led to this conclusion.

[27] Methods of calculating the magnitude and the frequencies of the potential fluctuations in ionized gases have been discussed by I. Langmuir, Proc. Nat. Acad. Sci. **14**,

Forces acting on an electron

A single electron located at a point A, at a distance x from a plane conducting surface S, is acted on by a force $e^2/4x^2$ drawing it toward the surface. This force is equal to that which would be exerted on the electron at A by an equal positive charge at the image A' and is therefore usually called the image force.

Let us now consider the force acting on an electron B in an ionized gas close to a plane metallic surface. We have seen in the foregoing section that the average potential V at any point P can be calculated from n by Poisson's equation. It should be noted, however, in this calculation that *no electron was assumed to be located at P*, that is, the probability per unit volume for the occurrence of an electron at P was taken to be the same as at other points in the neighborhood of P.

In order to calculate the force on the electron B we must now consider that the electron is definitely located at P. This introduces an unsymmetrical element which was entirely absent in our calcuation of n and V as average values. At P, the probability of the presence of an electron now becomes unity so that $n = \infty$ at this point. In a similar way $V = -\infty$ at P. It is customary to avoid this difficulty by ignoring the presence of the electron at P in calculating V. The force acting on the electron at P is then taken to be $e \, dV/dx$.

Although we can ordinarily properly ignore the effect of the electron at P in calculating, by means of Poisson's equation, the forces resulting from the action of all the other electrons and ions, it is clear that in this way we do not allow for the image force[28] corresponding to the image at P'.

628–37 (1928), especially pp. 632–4. See also L. Tonks and I. Langmuir, Phys. Rev. **33**, 195–210 (1929).

[28] In M. v. Laue's paper dealing with the potential distribution resulting from electron space charges in equilibrium with metal surfaces (Jahrb. d. Radioak. und Electronik **15**, 207 (1918)) he ignored the image force in some problems where this force is of vital importance. In a subsequent paper (ibid. **15**, 302 (1918)) he attempted to justify this omission by arguing that the ordinary space charge treatment includes the effect of the images. Schottky (Phys. Zeits. **20**, 220 (1919)) pointed out that this conclusion is justified for the images of all the electrons *except that of the electron on which the force is acting.* Later

Fowler[29] shows that a rigorous calculation of the distribution of electrons and ions near a surface would involve an averaging of the effects of all movable charges in the "assembly," including those within the metal. Since "such a procedure seems to be far beyond our resources at present, a correction is necessary for the polarizing effect of the individual ion (or electron) on the metal surface." A consideration of the image force $e^2/4x^2$ which constitutes just such a correction should give accurate results whenever we are justified in regarding the metal surface as an equipotential plane surface.

The forces acting on a given electron at P are of three types:

Type 1. The force $e(dV/dx)$ due to the *potential field* V as given by Eq. (48), or by Poisson's equation, from values of n_e and n_p obtained by ignoring the presence of the electron at P. Since n_e and n_p will be uniform over any plane parallel to S, Poisson's equation takes the form

$$d^2V/dx^2 = 4\pi e(n_e - n_p).\qquad(49)$$

Type 2. The *electric image force* $e^2/4x^2$ corresponding to the image at P'.

Type 3. The force that results from the *segregation of electrons* (or ions) in the neighborhood of P in accord with the Debye-Hückel effect. This force must also include that due to the *image of the segregation.* Because of this image effect, the displacements of the charges produced by the presence of the electron at P will not have spherical symmetry about P.

This rather arbitrary separation of the force into 3 parts has the advantage that it throws the whole difficulty of the calculation into the third part. If it can be shown under any given conditions that the forces due to segregation are negligible, the problem can usually be readily solved.

Potential and motive

Much confusion can be avoided by analyzing a little more closely the concept of electric poten-

tial when used to calculate the forces acting on an electron.

The general concept of potential (Newtonian) is that of a scalar quantity whose gradient is used to represent a vector field having no curl. We ordinarily conceive of a static electric field as a state of space which acts on a particle having a charge e to produce a mechanical force F which is proportional to e.

In order not to disturb unduly the distribution of neighboring charges, it is customary to postulate that the charge used to measure any given electric field shall be small.

Logically, therefore, the field intensity E should be measured by dF/de for $e = 0$. This definition is consistent with common usage in all ordinary cases.

The electric image force $e^2/4x^2$ which acts on an electron or ion near a plane conducting surface varies in proportion to the square of the charge and thus the value of dF/de is zero for $e = 0$. The image field which acts on the electron differs radically from ordinary electric fields in that its existence depends upon the presence of the electron upon which it acts. It is important to recognize clearly this distinction between these two types of field.

The vector field corresponding to the ordinary electrostatic field $(E = dF/dx$ for $e = 0)$ may be represented by the potential V. We may consider either the *instantaneous potential* V or the *average potential* $\overline{V}$. In the former case V can be determined by Eq. (46) or by Laplace's equation which must hold everywhere except inside of the electrons. The average potential $\overline{V}$ at a point P, which is usually of more interest to us, can be determined by Eq. (48), or by Poisson's Eq. (49), from the average values of n_e and n_p, excluding any effects due to the presence of an electron at P.

The image force which acts on an electron at any point P, because of the presence of any neighboring conductor, varies in magnitude and direction as P is moved throughout the available space. Thus the image force also corresponds to a vector field. Under equilibrium conditions this field will have no curl and may therefore be represented by a potential. However, this potential has very different characteristics from either V or $\overline{V}$. For example, it will not satisfy Laplace's equation, and if it is substituted into Poisson's

v. Laue (Sitzber. Preuss. Akad. d. Wiss. **32**, 340 (1923)) acknowledged the correctness of Schottky's criticism and added an excellent discussion of the true character of the image force.

[29] R. H. Fowler, *Statistical Mechanics* (1929), p. 283.

equation in order to calculate the space charge, values of ρ or n are found which are purely fictitious, having no relation to actual space charges present.

To avoid confusion it seems desirable to adopt different terminology in describing these various kinds of potential. It seems useful to reserve the term *potential*, in electrical problems, to represent the fields which may be supposed to exist in space independently of the presence of a charge on which they act. It has been proposed[30] that the potential of the vector field corresponding to the forces which act on an electron or ion be named the *motive*, as an abbreviation of what the electrochemist calls "electromotive force." The motive M is thus defined as a scalar quantity whose gradient in any direction and at any point represents the force component per unit charge which must be applied to an electron or ion to hold it in equilibrium at the given point. Thus each particle tends to move towards a point where the motive is a minimum.

The force F_e exerted by the motive field on an electron at the distance x from a plane conducting surface is thus

$$F_e = -dMe/dx = e(dV/dx) - e^2/4x^2, \quad (50a)$$

while on a univalent positive ion the force would be

$$F_p = -dM_p/dx = -e(dV/dx) - e^2/4x^2. \quad (50b)$$

By integration we thus obtain for an electron

$$M_e = -V - (e/4x) = -V$$
$$-3.575 \times 10^{-8}/x \text{ volts} \quad (51a)$$

and for a positive ion,

$$M_p = +V - (e/4x) = +V$$
$$-3.575 \times 10^{-8}/x \text{ volts.} \quad (51b)$$

In these equations e represents the numerical value of the electron charge, i.e., e is always taken to be positive.

The motive thus consists of two parts: one being the ordinary potential V and the other the *image motive* $-e/4x$. It should be noted that with the image motive no distinction need be drawn

between instantaneous and average values for they are identical. Since, however, there are these two kinds of potential, we must also distinguish between instantaneous and average values of the total motives M_e and M_p.

The essential differences between the image motive and the potential result from the fact that the former owes its origin to a displacement of electrons in the metal by the action of the electron at P. The fields set up by the segregation of electrons and ions around given ions in ionized gas, according to the Debye-Hückel theory, are clearly *motive fields* and not potential fields, since they also depend for their existence on the definite presence of a charged particle at a given point. We see then in accordance with our classification of the forces acting on an electron at a point P into 3 types, that the motive M_e will consist also of three parts: the *potential* $-V$, the *image motive* $-(e/4x)$ and the "*segregation motive.*"

Distribution of electrons and ions

Since the work done in moving a charged particle from one place to another is determined by the motive instead of the potential, it is clearly the motive that should occur in the exponent of the Boltzmann equation. Making this modification in Eq. (20) and introducing the value of the motive from Eq. (51) we obtain

and
$$\left. \begin{array}{l} n_e = n_0 \epsilon^{\eta} \epsilon^{x_s/x} \\[2mm] n_p = n_0 \epsilon^{-\eta} \epsilon^{x_s/x}, \end{array} \right\} \quad (52)$$

where x_s is a parameter having the dimensions of a length which we may call the *Schottky distance*.[31] Its value is

$$x_s = e^2/4kT = 4.149 \times 10^{-4}/T \text{ cm.} \quad (53)$$

Double differentiation of Eqs. (51) and combination with Poisson's Eq. (49) gives

$$\left. \begin{array}{l} d^2M_e/dx^2 = -4\pi e(n_e - n_p + n_F), \\[2mm] d^2M_p/dx^2 = -4\pi e(n_p - n_e + n_F), \end{array} \right\} \quad (54)$$

where
$$n_F = 1/(8\pi x^3) = 0.0398/x^3. \quad (55)$$

Comparison with Eq. (49) shows that the motive distribution is in accord with Poisson's

[30] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. A107, 68 (1925), and K. T. Compton and I. Langmuir, Rev. Mod. Phys. 2, 152 (1930).

[31] This parameter occurs in the equations first deduced by W. Schottky, Phys. Zeits. 15, 872 (1914).

equation only if we are willing to consider[32] a *fictitious space charge* en_F, whose effects thus replace those of the image force.

This form of expression has the advantage that it enables us to determine the relative importance of true space charge and image force (n_F) as factors determining the distribution of charged particles. If $|n_p-n_e|\gg n_F$, then the effects of the image force are negligible and our previous treatment which led to Eqs. (23) and (32) is adequate.

Since n_F increases very rapidly as x decreases, there must always be a region close to a metallic surface where n_F becomes much more important than n_p-n_e. We shall refer to this region as the *image sheath*.

Image sheath in neutral ionized gas

We may gain a clearer insight into the nature of the image sheath by considering the effect of image forces on an ionized vapor containing equal numbers of electrons and ions so that $n_e=n_p$. In this case even within the sheath there is no space charge and potential fields ($\bar{V}$) are absent so that the mathematical treatment is much simplified.

By putting $\eta=0$ in Eq. (52), the concentration of both electrons and ions is found to be

$$n = n_0 \epsilon^{x_s/x}. \tag{56}$$

The excess concentration $n-n_0$ integrated between two values of x, say x_1 and x_2 gives the sheath adsorption between these planes. Let us choose both x_1 and x_2 large compared to x_s; then we may expand the exponential and by integration obtain

$$\sigma = n_0 x_s [\ln (x_2/x_1)$$
$$+\tfrac{1}{2}x_s(x_2-x_1)/x_1 x_2+\cdots]. \tag{57}$$

If we let x_2 increase without limit, we see that the logarithmic term causes σ to approach ∞. This indicates that an image force varying inversely as x^2 falls off so slowly with increasing distance that it would cause an infinite total adsorption for a semi-infinite enclosure bounded by a plane metallic surface. This difficulty disappears if we consider the Debye-Hückel segregation. The range of the image force cannot exceed

[32] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. A107, 69 (1925).

a distance comparable with the Debye distance λ given by Eq. (2).

Debye and Hückel[12] have shown that the potential at a distance r from an ion in an ionized gas is

$$V=(e/r) \exp (-r/\lambda). \tag{58}$$

The attractive force F between a positive and a negative ion (or electron) at a distance r apart is thus

$$F=e\, dV/dr=(e/r^2)(1+r/\lambda) \exp (-r/\lambda). \tag{59}$$

The plane which is perpendicular to and bisects the line connecting the ions is an equipotential surface ($V=0$) and therefore may be replaced by a metallic conductor without altering the force F. Putting $r=2x$ in Eq. (59), where x is now the distance from one ion to the plane, we have for the image force acting on an ion in a neutral ionized gas

$$F= -(e^2/4x^2)(1+2x/\lambda) \exp (-2x/\lambda). \tag{60}$$

The motive M is then found by integration to be

$$M=(e/4x) \exp (-2x/\lambda). \tag{61}$$

For small values of x this does not differ appreciably from that given by Eq. (51). The sheath adsorption σ between x and ∞ is then given by

$$\sigma/n_0 = \int_x^\infty \{\exp [(x_s/x)\epsilon^{-2x/\lambda}]-1\}dx. \tag{62}$$

Although according to Eq. (2), λ is a function of n, it will remain substantially constant until x decreases to a value comparable with x_s, for by Eq. (56) n is also constant and equal to n_0 within this region.

When $x<x_s$, however, the exponent $2x/\lambda$ is very small compared to unity even after n has increased considerably, since $x_s\ll\lambda$. Thus in Eq. (62) we may take λ to be constant and equal to λ_0. If now $x\ll\lambda_0$ integration gives

$$\sigma/n_0 = x_s Ei(x_s/x)$$
$$-x_s \ln (2.334 x_s/\lambda_0)+x(1-\epsilon^{x_s/x}). \tag{63}$$

If we take $x\ll x_s$, which is the only region where there is appreciable adsorption, we can use the semiconvergent expansion for the

exponential integral Ei obtaining

$$\sigma/n_0 = (x^2/x_s) \exp(x_s/x) - x_s \ln(2.33 \, x_s/\lambda_0). \quad (64)$$

This equation gives the sheath adsorption caused by a plane metallic surface in contact with a neutral ionized gas, taking into account the Debye-Hückel segregation.

Let us now consider the conditions that must be fulfilled in order that $n_e = n_p$.

By dividing Eq. (13) by (14), the condition for equality of n_e and n_p is seen to be

$$\mu_e/\mu_p = 42.73 \, M^{1/2}. \quad (65)$$

Thus for caesium ($M = 132.8$) a neutral ionized vapor occurs if the amount of adsorbed caesium is such that the electron emission is 492 times as great as the ion emission. From equations based on Taylor's experimental data[6] we find that this value of the ratio of the emissions corresponds to a film for which the contact potential V (in volts) against a clean tungsten surface is given by

$$V = 2.754 - 2.50 \times 10^{-3} T$$

$$+ 9.24 \times 10^{-5} T \log_{10} \mu_a, \quad (66)$$

where T is the temperature of the tungsten surface. Taylor's data give an equation[6] which expresses μ_a as a function of T and σ, and also give V as a function of σ. For any given value of T we then have three equations for determining μ_a, V and σ.

In order to get a better idea of the magnitudes of the quantities involved, let us consider an enclosure at 1000°K containing such a pressure of caesium vapor that $n_e = n_p$. Putting $T = 1000$ and solving the three equations we find $\mu_a = 6.1 \times 10^{14}$ atoms cm^{-2} sec.$^{-1}$; $V = 1.621$ volts and $\sigma = 8.0 \times 10^{13}$ atoms per cm^2 of true surface which is 22.3 percent of the surface concentration corresponding to a completely covered surface.[33] To give this value of μ_a the caesium pressure at 1000°K must be 0.0084 barye and the atom concentration is $n_a = 6.13 \times 10^{10}$. This concentration of Cs will also be produced in an enclosure at 1000°K if this is connected to a bulb containing

saturated caesium vapor at 34°C (at which temperature the pressure is 0.00465 barye) since in this case also $\mu_a = 6.1 \times 10^{14}$.

By Eq. (9) we find at $T = 1000$ that $K = 2.29$ and thus by Eq. (22), placing $n_a = 6.13 \times 10^{10}$, the concentration of electrons and of ions in the enclosure is $n_0 = 3.75 \times 10^5$. Eqs. (13), (14) then give $\mu_e = 1.85 \times 10^{12}$ and $\mu_p = 3.74 \times 10^9$. Corresponding to these, the electron emission is 2.9×10^{-7} and the ion emission 6.0×10^{-10} ampere cm^{-2}, currents which are easily measurable.

By an analysis[8] of the experimental data it is also possible to deduce the following properties of the caesium film (at 1000° and $\theta = 0.223$). Let U be the heat of evaporation at constant pressure expressed in volts and defined in accord with the Clapeyron equation

$$U = -\frac{k}{e}\left(\frac{\partial \ln p}{\partial(1/T)}\right)_\theta = -\frac{k}{e}\left(\frac{\partial \ln \mu}{\partial(1/T)}\right)_\theta + \frac{1}{2}\frac{kT}{e}, \quad (67)$$

where $e/k = 11{,}606$ degrees per volt. The data give $U_a = 2.45$; $U_p = 3.32$; $U_e = 3.22$ volts. The ionizing potential, which has a temperature coefficient $(5/2)(k/e)$ is 4.09 volts at 1000°. These values satisfy Eq. (1). The spreading force F of the adsorbed film is 43.2 dynes cm^{-1} (of which 14.6 corresponds to the ideal two-dimensional gas law $F = \sigma kT$). The dipole moment M of the adatoms (which is related to the contact potential V by the relation $V = 2\pi\sigma M$) is $M = 10.87 \times 10^{-18}$.

For comparison with these data it is of interest to give those corresponding to very low values of σ where the atoms do not affect one another. In this case for $\sigma = 0$ at 1000° we find $U_a = 2.83$; $U_p = 2.09$; $U_e = 4.84$; $U_i = 4.09$. The dipole moment is $M = 16.2 \times 10^{-18}$.

Let us now apply Eq. (64) to calculate the adsorption within various parts of the image sheath for the case $T = 1000$, $\theta = 0.223$. From n_0 and T we find by Eq. (2) $\lambda_0 = 0.252$ cm. The Schottky distance x_s by Eq. (53) is $x_s = 4.15 \times 10^{-7}$ cm. The total adsorption beyond $x = 10^{-7}$, according to Eq. (64), amounts to only $\sigma = 2.5$ ions and electrons per cm^{-2}. For $x = 5 \times 10^{-8}$ cm this has increased to 910, and to 93,000 at $x = 3 \times 10^{-8}$. To give the observed value $\sigma = 8.0 \times 10^{13}$ for the total adsorbed caesium we should have to place $x = 1.15 \times 10^{-8}$ cm.

Of course at such small distances from the sur-

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[33] In Taylor's experiments 0.5 percent of the tungsten surface was found to adsorb caesium much more strongly than the rest. The values of σ and the covering fraction θ used in the present paper are those corresponding to the homogeneous part (99.5 percent) of the surface.

face the concept of image force becomes rather indefinite. Let us, however, see what results are obtained by the application of the equations we have derived and later we shall discuss what modifications are needed to take into account the special conditions very near the surface of a metal.

The attractive forces which act on the ions and which hold them on the surface as an adsorbed film must be balanced by a pressure or by repulsive forces. In the image sheath, insofar as the Boltzmann equation is applicable, the pressure gradient balances the attractive force. But the forces of attraction which hold the ions in the adsorbed film on the surface must be balanced by repulsive forces of another kind, any accurate knowledge of which must involve quantum theory. Let us assume provisionally that the image force acting on these ions is still $e^2/4x$, but that this is balanced by a repulsive force which varies inversely with a much higher power of the distance. The repulsive forces then contribute only a small part to the potential energy of the adions and for the present we shall neglect them. Then the heat of evaporation of the ions U_p is equal to the change of motive as given by Eq. (51) or (61) so that

$$U_p = e/4x = 3.58 \times 10^{-8}/x \text{ volts.} \qquad (68)$$

Introducing the experimental value for U_p = 3.32, we find $x = 1.07 \times 10^{-8}$ cm in fair agreement with the value 1.15×10^{-8} obtained from the total image sheath adsorption by Eq. (64).

The dipole moment M should be related to x by the relation

$$M = 2ex = 9.54 \times 10^{-10}x. \qquad (69)$$

Substitution of the experimental value M = 10.87×10^{-8} gives $x = 1.15 \times 10^{-8}$ again in good agreement with that given by Eq. (64).

According to Eq. (64) the concentration of electrons and ions should increase equally as the surface is approached. The fact that the adsorbed caesium gives a film having a contact potential of 1.62 volts against clean tungsten proves that the concentration of ions must increase faster than that of the electrons. In other words the forces acting on the ions are greater than those acting on the electrons.

At these small distances it becomes important to know the location of the surface from which x is measured. We have so far considered that the metal acts as an idealized perfect conductor with a plane surface. Actually, however, as we shall see later from a consideration of Fermi's theory and of Nordheim's theory of the distribution of electrons near a metal surface there is an electron atmosphere of high concentration extending roughly 4×10^{-9} cm out beyond the potential barrier which may be thought of as the boundary of the metal. The "reflecting plane" analogous to that of the idealized conductor is thus located at a level at which the electron atmosphere has some definite concentration.

The effect of the presence of an ion near the surface may be to raise the level of this reflecting surface under the ion whereas an electron would depress the reflecting surface.

Image sheath in unipolar gas

If the particular relation between the electron and the ion emission from the surface needed to make $n_p - n_e$ is not fulfilled, then in general the sheath will contain only particles of one sign. Beyond the range of the image force the distribution is given by Eqs. (32) and (33). We now need to consider how these equations must be modified within the image sheath.

A complete solution of the problem, which may theoretically be obtained from Eqs. (54), (55) and (52), is in general not practicable. However, by making use of the fact that $x_s \ll x_L$ under all experimental conditions, it is possible to treat the problem in a simple way. By comparing Eqs. (33) and (53) we see that

$x_s \ll x_L$ whenever

$$n_1 \ll 8(kT)^3/\pi e^6 = 5.57 \times 10^8 T^3 \text{ cm}^{-3}. \qquad (70)$$

This condition is practically the same as that expressed by Eq. (5) for the nonformation of a condensed phase in a homogeneous ionized gas. Thus at temperatures of the order of 1000° this relation will always be fulfilled if n_1 is small compared to 10^{17} cm^{-3}, a value far higher than can be realized experimentally.

The second column of Table I gives values of x_L/x_s calculated from Eqs. (33) and (55) for a wide range of values of n_1.

Assuming then that $x_s \ll x_L$, we see by Eq. (32) that at distances from the surface comparable

with x_s space charge effects should cause no rapid change in n. The fictitious space charge n_F, however, increases extremely rapidly, by Eq. (55), as x decreases below x_s. Thus by Eq. (54) the motive M undergoes changes which are very large compared to those of the potential. This decrease in motive, corresponding to $-e/4x$ by Eq. (51), has the effect, according to Eq. (52), of increasing the concentration n by the factor exp (x_s/x). As x decreases still further, this exponential factor should finally cause n to increase until it again exceeds n_F which varies with x^{-3}. Thus very close to the surface, within the *image sheath*, there may be a *second* or *inner space charge sheath* in which potential changes again determine the distribution of concentration.

Between the two space charge sheaths the concentration may be calculated as though no abnormal changes in potential occurred. A general equation for n is thus obtained by multiplying the value of n given by Eq. (32) by this exponential factor. In this way after introducing the value of x_s from Eq. (53) we obtain

$$n = [\exp (x_s/x)]/[8\pi x_s(x+x_L)^2].   (71)$$

This equation should be applicable within the outer space charge sheath as well as the image sheath. In our further analysis of the conditions within the image sheath, we shall determine the magnitude of the errors introduced into this equation by the approximations we have made.

Definition of n_1. We have previously defined n_1 as the value of n at $x=0$. Now that we are taking the image force into account, we see that this definition is no longer permissible for n increases indefinitely as x approaches 0. This difficulty is the same as that met in defining the saturation electron emission from a hot metal. The saturation current density I_S corresponds to that theoretically obtainable if the accelerating field is reduced to zero and yet space charge effects are not present; conditions often incompatible with one another. In accord with Eqs. (13), (14) and (16), n_1 may be defined in terms of the saturation currents as follows. For electron sheaths where I_{se} is the electron saturation current in amperes cm^{-2}

$$n_1 = 4.044 \times 10^{13} I_{se} T^{-1/2} \text{ cm}^{-3}.   (72)$$

For positive ion sheaths where I_{sp} is the ion

saturation current (amperes cm^{-2})

$$n_1 = 1.728 \times 10^{15} I_{sp}(M/T)^{1/2} \text{ cm}^{-3}.   (73)$$

If we hesitate to attach a precise meaning to saturation currents where electric fields near the metal surface are unavoidable, we may logically look upon n_1 as a useful parameter (defined by Eqs. (32) and (71)) which depends only on the condition of the metallic surface.

Outer boundary of image sheath

We may take the effective boundary between the outer space charge sheath and the image sheath as the plane at x_F at which $n=n_F$, for by Eq. (54) this is the place where the image force and the actual space charge contribute equally to the motive distribution.

Putting $x=x_F$ in Eqs. (55) and (71) and eliminating n_F we get

$$x_s(x_F+x_L)^2 = x_F{}^3 \exp (x_s/x_F).   (74)$$

Under conditions realizable experimentally we shall find that x_F is large compared to x_s and therefore by expanding the exponential factor we obtain the equation

$$x_F{}^3 = x_s x_L(x_L+2x_F).   (75)$$

In Table I values of x_F/x_s calculated in this way from x_L/x_s are given in the fourth column. From the data in the fifth column the actual values of x_F for any temperature are obtainable. The sixth column, which contains n_F/n_1, shows that n_F and n_1 are nearly equal so that as an approximate definition of n_1 we may say that n_1 is the value of n at a plane at which $n=n_F$, that is, at the effective limit of the range of the image force.

Inner boundary of the image sheath

We may take this effective boundary between the image sheath and the inner space charge sheath to be the plane at which n again equals n_F. Let x_{FF} be the distance of this plane from the surface. From Eqs. (55), (71), (33) and (53) we obtain

$$(x_{FF}/x_s)^3 \epsilon^{x_s/x_{FF}} = (x_L/x_s)^2$$

$$= 8(kT)^3/\pi e^6 n_1 = 5.57 \times 10^8 T^3/n_1.   (76)$$

The relations between x_{FF} and other parameters characterizing the space charge and image

TABLE I. *The parameters which characterize the image sheath and the two space charge sheaths.*

1 n_1/T^3 (deg.$^{-3}$ cm^{-3})	2 x_L/x_s	3 Tx_L (cm deg.)	4 x_F/x_s	5 Tx_F deg. cm	6 n_F/n_1	7 x_{FF}/x_s	8 Tx_{FF} (deg. cm)	9 n_{FF}/T^3 (deg.$^{-3}$ cm^{-3})
10^{-10}	2.36×10^9	9.79×10^5	1.77×10^6	736.	0.9985	0.0181	7.51×10^{-6}	9.42×10^{13}
10^{-8}	2.36×10^8	9.79×10^4	3.82×10^5	159.	0.9968	0.0199	8.24×10^{-6}	7.15×10^{13}
10^{-6}	2.36×10^7	9.79×10^3	8.25×10^4	34.2	0.9930	0.0220	9.14×10^{-6}	5.24×10^{13}
10^{-4}	2.36×10^6	9.79×10^2	1.78×10^4	7.39	0.9849	0.0247	1.026×10^{-5}	3.71×10^{13}
10^{-2}	2.36×10^5	9.79×10	3.86×10^3	1.60	0.9675	0.0282	1.170×10^{-5}	2.49×10^{13}
1	2.36×10^4	9.79	842.	0.349	0.9334	0.0329	1.37×10^{-5}	1.56×10^{13}
10	7.46×10^3	3.10	395.	0.164	0.9042	0.0360	1.49×10^{-5}	1.20×10^{13}
10^2	2.36×10^3	9.79×10^{-1}	186.	7.74×10^{-2}	0.8638	0.0397	1.65×10^{-5}	8.93×10^{12}
10^3	7.46×10^2	3.10×10^{-1}	88.6	3.68×10^{-2}	0.8080	0.0443	1.84×10^{-5}	6.43×10^{12}
10^4	2.36×10^2	9.79×10^{-2}	42.7	1.77×10^{-2}	0.736	0.0502	2.08×10^{-5}	4.40×10^{12}
10^5	7.46×10	3.10×10^{-2}	20.9	8.67×10^{-3}	0.640	0.0583	2.42×10^{-5}	2.82×10^{12}
10^6	2.36×10	9.79×10^{-3}	10.5	4.36×10^{-3}	0.527	0.0699	2.90×10^{-5}	1.63×10^{12}
10^7	7.46	3.10×10^{-3}	5.52	2.29×10^{-3}	0.392	0.0886	3.68×10^{-5}	0.80×10^{12}
10^8	2.36	9.79×10^{-4}	3.10	1.29×10^{-3}	0.258	0.1259	5.22×10^{-5}	0.28×10^{12}

The quantity n_1 is the concentration of electrons or ions (per cm³) at the surface of the metal calculated on the assumption that there is no electric image force. The v. Laue distance x_L is defined by Eq. (33); the Schottky distance x_s by Eq. (53); x_F and x_{FF} locate the outer and inner boundaries of the image sheath as given by Eqs. (75) and (76); n_F and n_{FF} are the concentrations at x_F and x_{FF}.

sheaths are illustrated in columns 7, 8 and 9 of Table I. It is seen that in spite of the enormous range of variation of n_1 of 10^{18}, the values of x_{FF} at $T = 1000°$ lie within the relatively narrow range from 0.7×10^{-8} to 3.7×10^{-8} cm. Thus the inner space charge sheath can lie only within distances from the surface comparable with an atomic diameter. The last column of Table I gives the concentration n_{FF} at the distance x_{FF} from the surface. At 1000° these concentrations are of the order of magnitude of 10^{22}, comparable with that of electrons within the metal.

An analysis of the validity of these equations within such close proximity of the surface will be made in a following section.

The *motive distribution* within the space charge and the image sheath may be obtained from n as given by Eq. (71) by means of the Boltzmann equation which takes the form

$$M = (kT/e) \ln (n_0/n)$$

$$= 1.984\times10^{-4}T \log_{10} (n_0/n) \text{ volts.} \quad (77)$$

The *potential distribution* within the outer space charge and image sheaths can be obtained by integration of Poisson's equation, Eq. (45), after inserting the value of n from Eq. (71). Expanding the exponential factor and taking the limits of integration to be ∞ and x we obtain[34]

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[34] In these integrations some logarithmic terms occur which become infinite when $x = \infty$. If, however, as in the

the convergent series

$$\eta = \eta_1 - 2 \left(\frac{x_s}{x_L}\right)^2 \left[\frac{1}{3!\,2\cdot1}\frac{x_s}{x}\right.$$

$$\left. + \frac{1}{4!\,3\cdot2}\left(\frac{x_s}{x}\right)^2 + \cdots\right], \quad (78)$$

where η_1 corresponds to the potential at the surface calculated without image force.

When $x_s/x = 5$, this gives $\eta - \eta_1 = -1.51\,(x_s/x_L)^2$ which by Table I is an extremely small quantity. For example, with $T = 1000$, $n_1 = 10^{10}$, $\eta - \eta_1$ would be only $2.7 - 10^{-8}$ corresponding to only 2.3×10^{-9} volts. The potential changes between x_F and $0.2\,x_s$, which is far within the image sheath are thus entirely negligible.

For very large values of x_s/x greater than about 10, where the series of Eq. (78) converges too slowly, the following semi-convergent series (based on that used for the exponential integral $Ei\ x$) becomes more useful:

$$\eta = \eta_1 - \tfrac{1}{3}(x_s/x_L)^2 \epsilon^{x_s/x}[3!\,(x/x_s)^4$$

$$+ 4!\,(x/x_s)^5 + \cdots]. \quad (79)$$

By Table I we see that x_s/x_{FF} is a quantity of the order of magnitude of 30 and thus the first

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derivation of Eq. (64), we take into consideration the segregation and integrate out only to a distance comparable with x_L, we find that the logarithmic terms become negligible.

term in the bracket alone is needed to calculate the potential at x_{FF}. Comparison of Eqs. (76) and (79) then gives

$$V_{FF} = V_1 - (2kT/e)(x_{FF}/x_s).$$

The motive M_{FF} at x_{FF} is according to Eqs. (51) and (53)

$$M_{FF} = V_1 - (kT/e)(x_s/x_{FF}),$$

so that

$$(V_{FF} - V_1)/(M_{FF} - V_1) = 2(x_{FF}/x_s)^2.$$

Thus since x_{FF}/x_s is of the order of magnitude of 0.03 by Table I we see that the potential change through the whole image sheath from x_F to x_{FF} is only about 1/500th of the change in motive in the same distance. This conclusion indicates that the effects of space charge are wholly negligible within the image sheath and furnishes a justification of our derivation of Eq. (70) in which the concentration given by Eq. (32) was merely multiplied by exp (x_s/x).

III. A PERTURBATION METHOD FOR THE STUDY OF THE IMAGE FORCE

In order to understand the nature of the image force on an electron close to a metallic surface, it is important to know the effect of the electron atmosphere which must extend an appreciable distance beyond the atoms of the metal. The principles involved may be illustrated by considering the interactions of individual electrons within the space charge sheath. By application of the Fermi-Sommerfeld theory of electrons in metals and Nordheim's theory of the transmission of electrons through surface barriers, the theory may then be extended to the case of electrons very close to a metallic surface.

By combining the Poisson and Boltzmann equations in the case of an electron sheath we obtain

$$d^2\eta/dx^2 = (4\pi e^2 n_0/kT)e^\eta. \tag{80}$$

The electron distribution given by Eq. (32) represents a special solution of this equation for the boundary conditions $\eta = 0$ and $d\eta/dx = 0$ at $x = \infty$. The potential distribution corresponding to this case, given by

$$\exp(\eta_1) = (kT/2\pi e^2 n_0)(x + x_L)^{-2}, \tag{81}$$

may be obtained by integration of Eq. (80) or from Eqs. (30), (26) and (2).

Curve I of Fig. 1 shows the potential distribution obtained from this equation for the case that $\lambda_0 = 1$ cm and $x_L = 10^{-4}$ cm. The value of x_L is taken as the unit for expressing x. Thus the surface of the metal is located at $x = 0$.

Let us now consider the effect of introducing a small surface charge uniformly distributed over a plane P located at x_P. The potential at any point instead of being η_1 will now be changed to $\eta = \eta_1 + \delta$ as illustrated in Fig. 1 by curves II and III. By substituting $\eta_1 + \delta$ in place of η in Eq. (80), expanding $e^\delta = 1 + \delta$, and eliminating η_1 by Eq. (81) we obtain

$$d^2\delta/dx^2 = 2\delta/(x + x_L)^2. \tag{82}$$

The solution of this equation is

$$\delta = A(x + x_L)^2 + B(x + x_L)^{-1}, \tag{83}$$

where A and B are integration constants. The two branches II′ and III′ of the curve on opposite sides of P evidently have different values of A and B.

These perturbations in η produced by the charge at P become small at large distances. For $x > x_P$ it is clear that $\delta = 0$ at $x = \infty$ and therefore by Eq. (83) $A = 0$, but B can have any arbitrary small value. Thus if δ_3 represents the value of δ for $x > x_P$ (Curve III′) we have

$$\left. \begin{array}{c} \delta_3 = B(x + x_L)^{-1} \\[2mm] d\delta_3/dx = -B(x + x_L)^{-2}. \end{array} \right\} \tag{84}$$

and

On the other side of $P(x < x_P)$, the perturbations disappear at the surface of the metal so that $\delta_2 = 0$ at $x = x_L$ and thus Eq. (83) gives

$$B = -Ax_L^3 \quad \text{for} \quad x < x_P,$$

whence

$$\left. \begin{array}{c} \delta_2 = A[(x + x_L)^2 - x_L^3(x + x_L)^{-1}] \\[2mm] d\delta_2/dx = A[2(x + x_L) + x_L^3(x + x_L)^{-2}]. \end{array} \right\} \tag{85}$$

and

The charge on the plane P is subjected to a force per unit area or pressure p given by

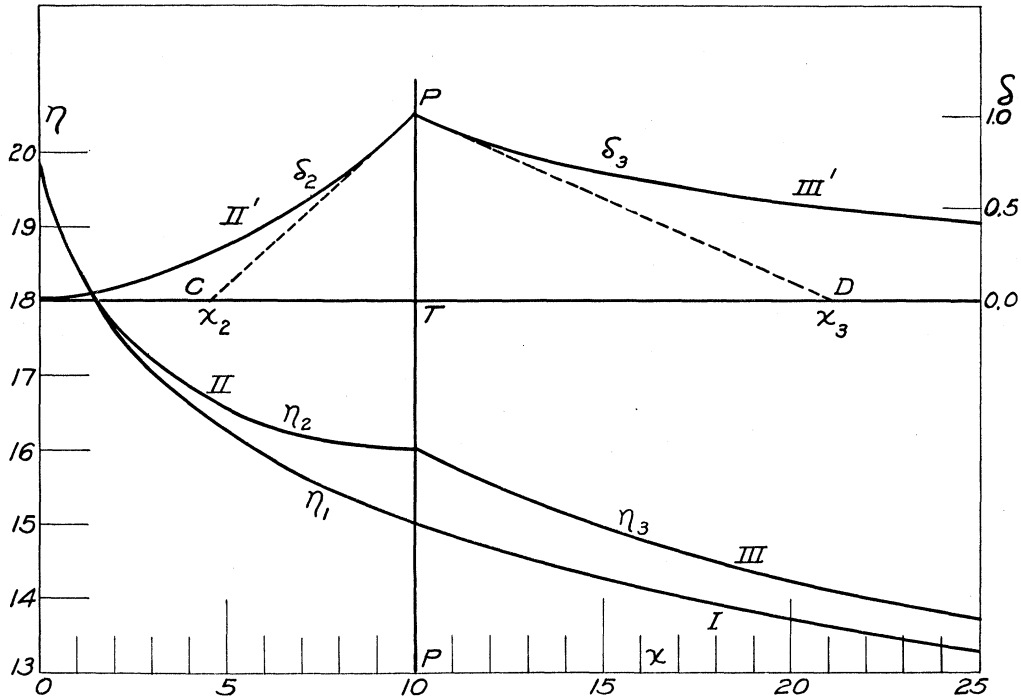$$8\pi(e/kT)^2 p = (d\delta_3/dx)_P^2 - (d\delta_2/dx)_P^2, \tag{86}$$

FIG. 1. Curves illustrating the perturbations in potential produced by a surface charge in
an electron atmosphere.

where the subscript P is used to indicate that the derivation is taken at x_P.

Let us now draw tangents to the curves II′ and III′ at the point P and continue these lines to their intersections C and D with the horizontal axis. Let x_2 and x_3 be the values of x at these points. Then we have

$$x_3 - x_P = -\delta_P/(\partial \delta_3/\partial x)_P = (x_P + x_L). \quad (87)$$

Similarly from Eq. (85), if we neglect $x_L{}^3$ compared to $(x_P + x_L)^3$ we find

$$x_P - x_2 = \delta_P/(\partial \delta_2/\partial x)_P = \tfrac{1}{2}(x_P + x_L). \quad (88)$$

If we do not neglect x_L in this calculation we obtain for $x_P = x_L$ a value 14/17 as great as that given above, while for the case that $x_P \lll x_L$ we find

$$x_2 = (2/3)x_P{}^3 x_L{}^{-2}. \quad (89)$$

The forces acting on the charges at P are thus the same as if the electron atmosphere which produces the field $\eta_1(x)$ were replaced by two conducting planes located at x_2 and x_3. The force experienced by each electron (or ion) at P may be regarded as due to the images of all the electrons

in P produced by the planes at x_2 and x_3. The total force on all the electrons on the plane P varies in proportion to the square of their number or the force on each one varies in proportion to the surface charge density. This is due to the fact that each electron is acted on not only by its own image but by the images of its neighbors in the plane P.

If we had a single electron on plane P, or if the electrons on P were at distances apart large compared to $x_P - x_2$ or $x_3 - x_P$, then the forces on each electron may be regarded as due to its images in two reflecting planes which are approximately at x_2 and x_3. An exact determination of positions of these reflecting planes for a single electron at P is a two-dimensional problem which will usually be beyond our mathematical resources. If we assume that the reflecting planes are at x_2 and x_3, we obtain for the force on a single electron

$$F = (e^2/4)[(x_3 - x_P)^{-2} - (x_P - x_2)^{-2}] \quad (90)$$

or by Eqs. (87) and (88)

$$F = -(3/4)e^2(x_P + x_L)^{-2}. \quad (90a)$$

By thus assuming that the reflecting planes for point charges are the same as for a distribution of charges over a plane, we fail to consider the segregation that occurs close to the point charge because of the high field strengths near the point. The error will evidently be negligible if the concentration of displacable charges near the plane P is small compared to that near the planes at x_2 or x_3. Although Eqs. (90) and (90a) are not exact, it is felt that they constitute very useful approximations which will not often cause errors of a serious nature. In a later section, in the derivation of Eq. (114), we shall have occasion to derive a more nearly exact expression for the image force on an electron near the boundary of a uniform plasma and shall compare it with an equation derived in the manner used for Eq. (90). This will serve to illustrate the degree of accuracy to be expected from Eq. (90).

Comparison of Eq. (90a) with the ordinary image force $-(1/4)e^2 x_P{}^{-2}$ shows that when $x_P \gg x_L$, the effect of the electrons or ions in the space charge sheath is to exert on each electron an image force three times as great as that normally given by the metallic surface. Because of the perturbations produced by an individual electron on the motions of neighboring electrons, the electron does not induce an image in the metal but induces two virtual images in the sheath.

We have seen, however, that the image force becomes appreciable as a factor in determining the distribution of changes in the sheath only at distances less than x_F, and the effects of the image force are important only at distances comparable with x_s. Table I, columns 2, 3, and 5 show that x_F and x_s are small compared to x_L. By Eq. (89) we find for $x_P = 0.1\ x_L$ that $x_2 = 0.007\ x_P$ and thus conclude that even in the image sheath the space charge effects we have been considering are of no practical importance in modifying the image force. The principles involved in these calculations, however, will be useful in considering conditions very near the surface within the image sheath where the concentration gradients of the electron atmosphere reach enormous values.

Free path of perturbations

According to the Debye-Hückel theory, a disturbance in potential in a plasma produces perturbations which decrease with the distance in proportion to exp $(-r/\lambda)$ where λ is given by Eq. (2). By analogy with the free paths of molecules in a gas we may thus regard λ as the mean free path of perturbations in a plasma or $1/\lambda$ is the absorption coefficient of plasma perturbations.

Let us consider, for example, the effect of placing a small uniform surface charge on a plane surface P within an infinite plasma. The potential at P is thus raised by an amount δ_P but elsewhere at a distance x from the plane the potential is

$$\delta = \delta_P \exp\ (-x/\lambda). \qquad (91)$$

The potential gradient close to P $(x = 0)$ which is δ_P/λ is the same as though the plasma were replaced by two conducting surfaces one on each side of P and at the distance λ from it. We may thus consider that each electron in the plane P is acted on by two image forces of magnitude $e^2/4\lambda^2$ which act in opposite directions and thus balance. The distance λ may also be regarded as the distance at which δ has fallen to $1/\epsilon$th value.

In the space charge sheath where there are large concentration gradients we have seen that potential perturbations gradually decrease (see Fig. 1) as the distance from the disturbance increases and that this rate of decrease is greater in regions of high concentration. We may inquire whether in such cases it is useful to consider that there is an *absorption* of the perturbations corresponding to a definite free path.

In presence of a concentration gradient the free path λ_F can no longer be identified with λ as given by Eq. (2). We may consider, however, that the absorption coefficient is equal to $1/\lambda$ where

$$\lambda = (kT/4\pi e^2 n)^{1/2} = 9.792\ (T/n)^{1/2}\ \mathrm{cm}^{-1} \quad (92)$$

and then as before may define the free path λ_F as the distance at which δ/δ_P is $1/\epsilon$. When λ varies with x, Eq. (91) is not applicable but instead we have

$$d \ln \delta/dx = -1/\lambda. \qquad (93)$$

Integration gives $\ln\ (\delta/\delta_P) = -\displaystyle\int_{x_P}^{x} (1/\lambda)dx.$

Putting $\delta/\delta_F = 1/\epsilon$ and $x = x_3$ or x_2 in accord with Fig. 1 we obtain

$$\int_P^{x_3} \lambda^{-1}dx = 1 \quad \text{or} \quad \int_{x_2}^{x_P} \lambda^{-1}dx = 1 \quad (94)$$

and the free path λ_F is then $\lambda_F = x_3 - x_P$ or $\lambda_F = x_P - x_2$.

Let us now apply this method to calculate λ_F within the space charge sheath and compare the results with those given by Eqs. (87) and (88). From Eqs. (92) and (32)

$$\lambda = 2^{-1/2}(x + x_L). \quad (95)$$

Substituting this in Eqs. (94), we find

$$\begin{rcases} x_3 - x_P = [\exp(2^{-1/2}) - 1](x_P + x_L) \\ \text{and} \\ x_P - x_2 = [1 - \exp(-2^{-1/2})](x_P + x_L) \end{rcases} \quad (96)$$

or combining with Eq. (95) and introducing the numerical value of $\exp(2^{-1/2}) = 2.0281$,

$$x_3 - x_P = 1.0281\ (2)^{1/2}\ \lambda_P \quad \text{and}$$

$$x_P - x_2 = 1.0139\ (2)^{-1/2}\ \lambda_P, \quad (97)$$

while Eqs. (87) and (88) give

$$x_3 - x_P = 2^{1/2}\ \lambda_P \quad \text{and} \quad x_P - x_2 = 2^{-1/2}\ \lambda_P. \quad (98)$$

Thus, although the method of calculating the location of the reflecting planes involving the concept of perturbation free path does not give a result identical with that of the "exact" method, the errors resulting when it is applied to the space charge sheath are relatively small (less than 3 percent).

The free path method, although only approximate, is useful because of its wide applicability even in cases where mathematical difficulties prevent the use of the exact method. There are some cases, however, where the concentration varies with x in a discontinuous manner, in which the free path method may fail more or less completely as illustrated by the example in the following section.

The concept of perturbation free path λ may often be applied usefully to electron or ion distributions which are not of the Maxwellian type. Thus we may interpret Eq. (92) as indicating that in general λ varies inversely as the square root of the concentration of perturbable par-

ticles and in proportion to the square root of their average kinetic energy L so that

$$\lambda = (L/6\pi e^2 n)^{1/2} \quad (99)$$

may be applied at least approximately to non-Maxwellian distributions.

IV. IMAGE FORCES NEAR THE BOUNDARY OF A PLASMA

Potential distribution

If we consider a semi-infinite region (bounded by a plane surface S, see Fig. 2) which contains both electrons and ions in thermal equilibrium at temperature T, we obtain in place of Eq. (80) the following equation for the potential distribution

$$d^2\eta/dx^2 = (\sinh \eta)/x_0^2, \quad (100)$$

where in accord with Eq. (2)

$$\lambda_0 = (kT/8\pi e^2 n_0)^{1/2}. \quad (101)$$

In the case of a typical plasma in which the concentrations of electrons and ions are nearly equal, the deviations δ from the normal plasma
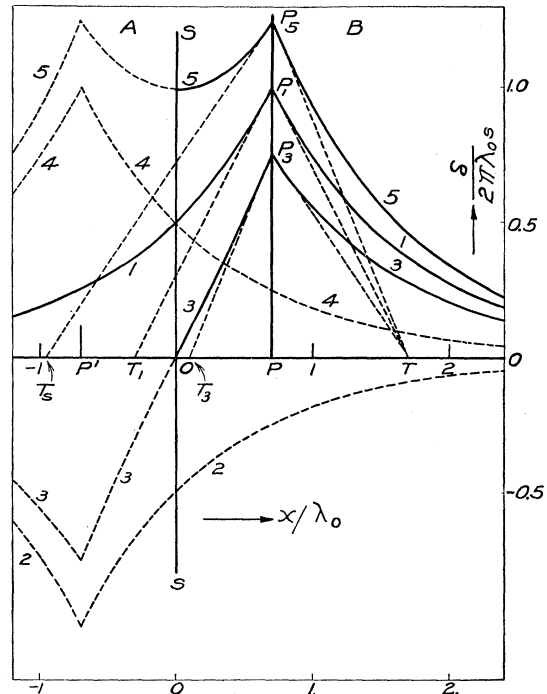

FIG. 2. Potential distributions produced by a surface charge in a plasma near the plasma boundary.

potential ($\eta = 0$) are small so that Eq. (100) becomes

$$\lambda_0^2 d^2\delta/dx^2 = \delta. \qquad (102)$$

Integration gives

$$\lambda_0^2 (d\delta/dx)^2 = \delta^2 + A, \qquad (103)$$

where A is an integration constant.

If $d\delta/dx = 0$ for $\delta = 0$, $A = 0$ and a second integration gives

$$\delta = \delta_0 \exp(\pm x/\lambda_0). \qquad (104)$$

This is the case already considered by Debye and Hückel which led to Eq. (91). It corresponds to the case where a disturbing charge is located at an infinite distance from the plasma boundary.

The curve 1 in Fig. 2 illustrates the potential distribution as given by Eq. (104) when a surface charge, or uniform surface density s, is placed on a plane surface P. The two branches of the curve which meet at P_1 correspond to different values of the integration constant δ_0. The slopes of the curve at P_1, being related to the surface charge density s, enable us to eliminate δ_0 and we so obtain.

$$\delta = 2\pi\lambda_0 s \exp(-\xi/\lambda_0), \qquad (105)$$

where

$$\xi = |x - x_P|. \qquad (106)$$

Boundary conditions

When $A \neq 0$ we have two integration constants to determine from the conditions existing at the plasma boundary.

To make our treatment more general let us consider that the plane S is the boundary between two plasmas A and B for which the values of n_0 are different. For example, B may be taken to be a gaseous plasma containing ions and electrons with moderate concentrations, while A may be a metal which, because of the free electrons and ions contained in it, may for the present purposes be regarded as a plasma of extremely high concentration. On the other hand, we may also take a case in which the concentration in A is zero as it would be, for example, if we take B to be a gaseous plasma bounded at S by a nonconducting surface such as a glass wall.

We shall reserve for a later section (Part 2) a consideration of the conditions at S which enable the two plasmas to be in equilibrium. For the present we need only point out that we shall have two limiting cases to consider when $n_A \gg n_B$ and when $n_A \ll n_B$. We wish in both cases to consider the forces which act on a charge at P in plasma B located near the boundary S.

The electric field surrounding the charge at P dies away at greater distances by a kind of absorption. The residual field which reaches as far as S acts to cause a displacement of the electron and ion atmospheres with respect to one another which results in a surface charge on S. For example, if the ion and electron concentration in A is very large compared to that in B, a negative charge at P tends to induce a positive charge on S which, in the limiting case, will prevent the field from extending an appreciable distance into A and make S an equipotential surface corresponding to $\delta = 0$ (Case I).

On the other hand (Case II), with $n_A \ll n_B$, there is a tendency for a negative charge at P to displace the electrons near S out into A, which is equivalent to inducing a *negative* charge in the surface S. In the limiting case this may go so far as to neutralize the field at S originating from P so that as a boundary condition at S we have $d\delta/dx = 0$.

Case I. $n_A \gg n_B$; $\delta = 0$. Since in this case the value of $d\delta/dx$ at $\delta = 0$ cannot be imaginary, we see by Eq. (103) that $A > 0$. Integration then gives the result that between 0 and P, δ varies in proportion to $\sinh(x/\lambda_0)$ as shown by the full line $0P_3$ in Fig. 2. In plasma A there will be no appreciable potential gradient; the resulting discontinuity in the slope of the potential curve indicates that the effect of the charge at P is to induce a surface charge of opposite sign at S.

The potential distribution in plasma B is evidently the same as if, instead of considering a boundary at S, we assume the concentration in A is the same as in B, but assume also that there exists at P' a surface charge of density $-s$. From symmetry we see that the condition $\delta = 0$ at $x = 0$ is then fulfilled. The potential distribution as shown by curve 3 in Fig. 2 is thus obtained by adding the potential given by curve 1 to that of the image P' as given by curve 2. Thus from Eq. (105) we have for the whole of curve 3,

$$\delta_3 = 2\pi\lambda_0 s [\exp(-\xi/\lambda_0) - \exp(-\xi'/\lambda_0)], \qquad (107)$$

where ξ and ξ' are the absolute values of the distances from P and P'. Between 0 and P, i.e., for $x < x_P$, after applying Eq. (106), this becomes

$$\delta_3 = 4\pi\lambda_0 s \exp\left(-x_P/\lambda_0\right) \sinh\left(x/\lambda_0\right), \quad (108)$$

while beyond P, for $x > x_P$, we have

$$\delta_3 = 4\pi\lambda_0 s \exp\left(-x/\lambda_0\right) \sinh\left(x_P/\lambda_0\right). \quad (109)$$

Curve 3 in Fig. 2 was calculated from these equations for the case that $x_P/\lambda_0 = 0.7$.

Image forces

If we draw tangents to curves 1 and 3 at the points P_1 and P_3, as indicated by the dotted lines, and determine their intersections T, T_1, and T_3 with the horizontal axes in accord with Eqs. (87) and (88), we obtain the locations of the "reflecting planes." Thus letting x_T, x_1 and x_3 be the abscissas at T, T_1 and T_3, we have

$$x_T - x_P = x_P - x_1 = \lambda_0 \quad (110)$$

and

$$x_P - x_3 = \lambda_0 \tanh\left(x_P/\lambda_0\right). \quad (111)$$

In accord with Eq. (86) we may now calculate the force or pressure p exerted by these fields on the charges at the plane P. For Case I corresponding to P_3 we find

$$P_3 = -2\pi s^2 \exp\left(-2x_P/\lambda_0\right). \quad (112)$$

We may now calculate by Eqs. (90), (110) and (111) the force that would act on a single electron located in the plane P (in the absence of a uniform charge on P).

$$F_3 = -(e/2\lambda_0)^2 \operatorname{csch}^2\left(x_P/\lambda_0\right). \quad (113)$$

It should be noted that this equation was derived by the same method that was used for Eq. (90) *viz.*, by assuming that the reflecting plane for a point charge is the same as that for charges uniformly distributed on a plane.

In the present case with a uniform plasma we do not need, however, to make this simplifying assumption. In fact, in Eq. (60) we already have an exact solution of the problem of the force on an electron near the boundary of a plasma (exact, if we can assume the validity of Eq. (102)). This equation may be written

$$F = -(e/2\lambda_0)^2 \epsilon^{-2\theta}(1+2\theta)/\theta^2, \quad (114)$$

where

$$\theta = x_P/\lambda_0. \quad (115)$$

Substituting Eq. (115) in Eq. (113), expanding in powers of θ and comparing with a similar expansion of Eq. (114), we have

$$F_3 = -(e/2\lambda_0)^2(1/\theta^2)$$
$$\times \left[1 - (1/3)\theta^2 + (1/15)\theta^4 \cdots\right] \quad (116)$$

and

$$F = -(e/2\lambda_0)^2(1/\theta^2)$$
$$\times \left[1 - 2\theta^2 + (8/3)\theta^3 \cdots\right]. \quad (117)$$

For large values of θ we can put in Eq. (113) $\operatorname{csch}\theta = 2\exp\left(-\theta\right)$ and thus from Eq. (114) find that

$$F/F_3 = (1+2\theta)/4\theta^2. \quad (118)$$

These equations enable us to estimate the magnitude of the errors introduced by the assumption, used in deriving Eq. (90), that the location of the reflecting plane for point charges is the same as for charges distributed over a plane. Serious errors are likely to occur only when a large fraction of the lines of force emanating from an electron fail to reach the reflecting plane S because of segregation in plasma B.

Case II. $n_A \ll n_B$; $d\delta/dx = 0$. This condition is the same as if we replace the plasma A by one having the same concentration as B, but assume that at P' there exists a surface charge of density $+s$. The potential distribution as illustrated by curve 5 is obtained by adding the potentials as given by curve 1 and its image (curve 4). By Eq. (105) we thus have for curve 5

$$\delta_5 = 2\pi\lambda_0 s\left[\exp\left(-\xi/\lambda_0\right) + \exp\left(-\xi'/\lambda_0\right)\right]. \quad (119)$$

Between 0 and P, for $x < x_P$, this gives

$$\delta_5 = 4\pi\lambda_0 s \exp\left(-x_P/\lambda_0\right) \cosh\left(x/\lambda_0\right) \quad (120)$$

and for $x > x_P$

$$\delta_5 = 4\pi\lambda_0 s \exp\left(-x/\lambda_0\right) \cosh\left(x_P/\lambda_0\right). \quad (121)$$

Proceeding as in the derivation of Eq. (111) we find

$$x_P - x_5 = \lambda_0 \coth\left(x_P/\lambda_0\right). \quad (122)$$

The pressure on the plane P calculated by Eq. (86) comes out to be the same as that given

by Eq. (112) except that the sign before the second member is reversed.

Using Eq. (90) to calculate the force F_5 on a single electron at P we obtain

$$F_5 = +(e/2\lambda_0)^2 \operatorname{sech}^2 (x_P/\lambda_0), \qquad (123)$$

whereas by the method that led to Eq. (60), considering the repulsion between two charges of like sign, we again get Eqs. (114) and (117), but with their signs reversed. From Eq. (123) for small values of θ we have

$$F_5 = +(e/2\lambda_0)^2[1 - \theta^2 + (2/3)\theta^4 \cdots]. \qquad (124)$$

Comparing this with Eq. (123) we see that F_5 and F do not agree at all for small values of θ. Of course, if $d\delta/dx$ is actually 0 at $x=0$, the value of $-F$ given by Eq. (123) should be correct. Eq. (124) corresponds more nearly to a case in which the surface charge at S is zero: a case which will usually be approximately fulfilled when an electron is near the boundary of a plasma. In Part II we shall find cases when both of these equations are applicable. A more definite knowledge is needed of the conditions which determine the equilibrium of the electrons and ions near the plasma boundary, before a proper choice of the equations can be made.

In any case, it is clear that when two plasmas having different concentrations are separated by a bounding surface, each charged particle near the boundary, but in the more dilute plasma, is acted on by an image force which tends to draw it towards the boundary. In the more concentrated plasma, however, the image force on a particle near the boundary tends to repel it from the boundary. Under equilibrium conditions these image forces are balanced by the potential gradients due to space charges and by the pressure gradients of the electron and ion atmospheres.

V. ELECTRONS WITH A FERMI DISTRIBUTION

Electron sheath inside the metal

For electron concentrations greater than 10^{21} at temperatures up to 1000° the electron gas is nearly completely degenerate. For this case Fermi[35] has shown that the distribution of elec-

[35] E. Fermi, Zeits. f. Physik 36, 902 (1926), and ibid. 48, 73 (1928).

trons in a field of force is given by

$$n = (2^{9/2}\pi m^{3/2}e^{3/2}/3h^3) V^{3/2}, \qquad (125)$$

where V is the potential at any point. Expressing V in volts

$$n = 4.602 \times 10^{21} V^{3/2} \text{ cm}^{-3}. \qquad (126)$$

At any point the kinetic energies of the electrons range from 0 up to V electron-volts, the average energy being $(3/5)V$.

Many of the features of a metal may be represented by a model consisting of a plasma containing an electron Fermi gas imbedded in a positive continuum of equivalent charge.

The distribution of potential and electron concentration in the plasma can now be obtained by combining Eq. (125) with Poisson's equation giving

$$\lambda_1^2(d^2\varphi/dx^2) = \tfrac{2}{3}(\varphi^{3/2} - 1) \quad \text{for } x < 0, \qquad (127)$$

where φ is a dimensionless variable proportional to V defined by

$$\varphi = V/V_1, \qquad (128)$$

where V_1 is the "inner potential" which is related to the electron concentration n_1 in the metal as follows,

$$V_1 = 2.452 \times 10^{-4} n_1^{1/6}. \qquad (129)$$

This is obtained from Eq. (126) by putting $n = n_1$ and solving for V. The parameter λ_1 in Eq. (127) has the dimensions of a length and is

$$\lambda_1 = \frac{2^{1/4}}{8\pi} \frac{h^{3/2}}{e^{5/4}m^{3/4}V_1^{1/4}} = 0.898 \times 10^{-8} V_1^{-1/4} \text{ cm} \qquad (130)$$

or if use is made of Eq. (125) λ_1 may be expressed in the simpler form

$$\lambda_1 = (1/4\pi)(\pi/3)^{1/6}(h/em^{1/2}n_1^{1/6})$$
$$= 3.662 \times 10^{-5} n_1^{-1/6} \text{ cm}. \qquad (131)$$

In order to determine the perturbations in the plasma potential produced by a disturbing charge on a plane P which lies within the plasma parallel to the bounding surface S (see Fig. 1) we may put in Eq. (127) $\varphi = 1 + \delta$, and so obtain

$$\lambda_1^2(d^2\delta/dx^2) = \delta. \qquad (132)$$

Since this is identical with Eq. (102), we may

apply Eqs. (108) to (113) without change to the present case. When the free path method is applicable, the parameter λ_1 as given by Eqs. (130) or (131) is thus the perturbation free path in a Fermi plasma.

Fermi sheath outside of a metal surface

The electron pressure in the metal must be balanced by forces acting on the electrons near the plasma boundary. These forces are of two kinds: electric forces due to the potential drop in a double sheath and image forces acting on the electrons within this sheath. Let us postpone the consideration of the image forces to a later section.

In accord with the model we have adopted we consider the surface of the metal to be the plane S which bounds the positive ion continuum. For $x<0$, Eq. (127) applies, but for $x>0$, since the positive charge is absent, the equation becomes

$$\lambda_1^2(d^2\varphi/dx^2) = \tfrac{2}{3}\varphi^{3/2}, \quad \text{for } x>0 \text{ and } \varphi>0. \quad (133)$$

We see from Eq. (125) that n falls to 0 at $V=0$ and therefore

$$d^2\varphi/dx^2 = 0 \quad \text{for } \varphi<0. \quad (134)$$

The potential distribution obtained by inte-

grating these equations with various boundary conditions are shown in Fig. 3.

We shall wish to consider the conditions at the surface when an approaching electron exerts a large force on the electrons in the sheath. This external field may be taken into account by considering that for $\varphi<0$, $dv/dx=E$ or

$$\lambda_1(d\varphi/dx) = E\lambda_1/V_1 \equiv -\beta \quad \text{for } \varphi<0, \quad (135)$$

where β is a dimensionless parameter.

The curves in Fig. 3 were calculated for $\beta=0$ and for various positive values of β corresponding to external retarding fields acting on electrons leaving the metal.

We may now integrate Eqs. (127) and (133) subject to the conditions $d\varphi/dx=0$ at $\varphi=1$ and $\lambda_1 d\varphi/dx=\beta$ at $\varphi=0$ and so obtain

$$\lambda_1^2(d\varphi/dx)^2 = (8/15)\varphi^{5/2} - (4/3)\varphi + 4/5$$

$$\text{for } x<0 \quad (136)$$

and

$$\lambda_1^2(d\varphi/dx)^2 = (8/15)\varphi^{5/2} + \beta^2$$

$$\text{for } x>0 \text{ and } \varphi>0. \quad (137)$$

At $x=0$ the values of $d\varphi/dx$ given by these two equations must be equal. Let φ_S be the value
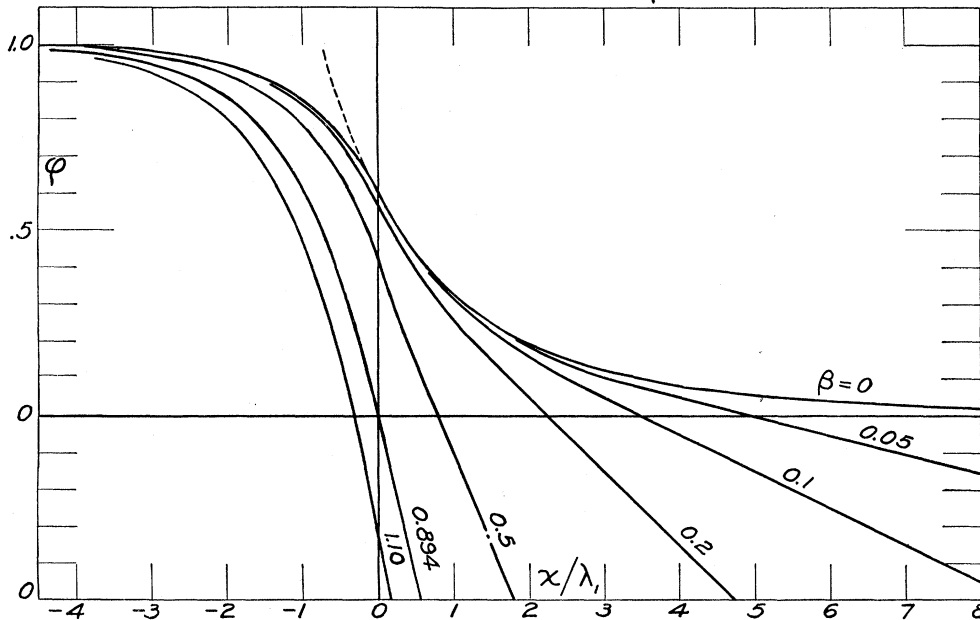

FIG. 3. Potential distribution in the Fermi sheath.

of φ at the bounding surface $S(x=0)$, then

$$\varphi_S = 3/5 - (3/4)\beta^2. \qquad (138)$$

Within the metal for $x<0$, we put $\varphi=1+\delta$ in Eq. (136), expand in powers of δ, and integrate, determining the integration constant by the condition $\delta=\delta_s=\varphi_s-1$ at $x=0$ and so obtain

$$x/\lambda_1 = \ln(\delta/\delta_s) - (1/12)(\delta-\delta_s)$$
$$+ (1/96)(\delta^2-\delta_s^2). \qquad (139)$$

This series converges sufficiently rapidly to give the potential distribution even when $\varphi_s=0$ or $\delta_s=1$.

For $x>0$ we must consider several cases.

Case I. $\beta=0$. Integration of Eq. (137) with the boundary condition $\varphi=\varphi_s$ at $x=0$ gives

$$x/\lambda_1 = (30)^{1/2}\varphi^{-1/4} - 6.224 \qquad (140)$$

or

$$\varphi = 900\lambda_1^4(x+6.224\lambda_1)^{-4}$$
$$= 0.6(1+x/6.224\lambda_1)^{-4}. \qquad (141)$$

By means of Eqs. (130) and (128) this may be expressed

$$V = 1800(8\pi)^{-4}h^6e^{-5}m^{-3}(x+6.224\lambda_1)^{-4}$$
$$= 5.85\times10^{-26}(x+6.224\lambda_1)^{-4} \text{ volts}. \qquad (142)$$

Thus when $\beta=0$ the potential in the sheath of Fermi gas outside the metal varies inversely as the fourth power of the distance from a plane inside the metal located at $x=-6.224\lambda_1$. The constant factor is a universal constant. The electron concentration varies inversely as the sixth power of this distance. The data for the curves marked $\beta=0$ in Fig. (3) were calculated by Eqs. (139) and (140).

Case II. $\beta^2<0.8$. When β has positive values, the curve giving $\varphi(x)$ crosses the X axis at some point x_0. Integration of Eq. (137) gives

$$x_0/\lambda_1 = I_S \text{ where}$$

$$I_S = \int_0^{\varphi_s} d\varphi[(8/15)\varphi^{5/2}+\beta^2]^{-1/2}. \qquad (143)$$

Let us put

$$I_S = I_\infty - (I_\infty - I_S), \qquad (144)$$

where I_∞, the definite integral obtained by putting ∞ in place of φ_s in Eq. (143), can be calcu-

lated in terms of gamma-functions and is found to have the value

$$I_\infty = 6.124\beta^{-1/5}. \qquad (145)$$

Expanding the integrand of Eq. (143) in powers of $\beta^2\varphi_s^{-5/2}$ and integrating we get

$$I_\infty - I_S = 30^{1/2}\varphi_s^{-1/4}$$
$$\times(1-0.0853\beta^2\varphi_s^{-2.5}+0.062\beta^4\varphi_s^{-5}\cdots) \qquad (146)$$

which converges rapidly when $\beta<0.3$.

For small values of β, where by Eq. (138) $\varphi_s=0.6$, Eq. (146) gives $I_\infty-I_S=6.224$. For $\beta=0.3$ this increases only about 2 percent. Thus by Eqs. (143), (144) and (145) for values of β up to 0.3 or 0.4 we have

$$x_0/\lambda_1 = 6.124\beta^{-1/5} - 6.224. \qquad (147)$$

A different expansion of Eq. (137) gives

$$(x_0-x)/\lambda_1 = (\varphi/\beta)$$
$$\times[1-(8/105)\beta^{-2}\varphi^{5/2}+(4/225)\beta^{-4}\varphi^5]. \qquad (148)$$

When $\beta>0.5$ this may be used for calculating x_0 by putting $x=0$ and $\varphi=\varphi_s$.

Case III. $\beta^2>0.8$. When β^2 reaches 0.8, Eq. (138) shows that φ_s becomes zero. For larger values of β the electron concentration falls to zero at some point within the metal, that is, $x_0<0$.

For $x<x_0$ the potential distribution is obtained from Eq. (139) by putting $\delta_s=1$ and replacing x by $x-x_0$.

The effect of these strong fields is to displace the electron distribution without changing the shape of the curve $\varphi(x)$. At x_0 the potential gradient is given by

$$\lambda_1(d\varphi/dx)_0 = -(0.8)^{1/2} = -0.894, \qquad (149)$$

which is the same as that outside the metal when $\beta=0.894$ and $\varphi_s=0$.

When $\beta^2>0.8$ there are no electrons between $x=x_0$ and $x=0$ so that Eq. (127) reduces to

$$\lambda_1^2(d^2\varphi/dx^2) = -2/3. \qquad (150)$$

At $x=0$ we must have $\lambda_1 d\varphi/dx = -\beta$ and at x_0, $\varphi=0$. Integration thus gives

$$\varphi = -\beta(x-x_0)/\lambda_1 - \tfrac{1}{3}(x^2-x_0^2)/\lambda_1^2$$
$$\text{for } x_0<x<0. \qquad (151)$$

Solving Eqs. (149) and (151) for x_0 we find that the displacement of the electrons is given by

$$x_0/\lambda_1 = (3/2)(0.894 - \beta). \qquad (152)$$

Substituting this in Eq. (151), placing $x = 0$, and comparing with Eq. (138) we find that this equation is still applicable when $\beta^2 > 0.8$.

Perturbations and image forces within the Fermi sheath

Putting $\varphi = \varphi_1 + \delta$ in Eq. (133), the perturbations in the Fermi sheath outside the metal are seen to be governed by the equation

$$\lambda_1{}^2(d^2\delta/dx^2) = \varphi_1{}^{1/2}\delta, \qquad (153)$$

where φ_1 is a function of x which represents the potential distribution in the undisturbed state as obtained by the solution of Eq. (133). In general Eq. (153) cannot be readily integrated.

Case I. $\beta = 0$. For this case by substituting the value of φ_1 from Eq. (141) into Eq. (153) and integrating we find

$$\delta = A(x + 6.22\lambda_1)^6 + B(x + 6.22\lambda_1)^{-5}. \qquad (154)$$

This may be handled in the same manner as Eq. (83). If the point P (see Fig. 1) is sufficiently far from the surface S so that δ_2 has fallen practically to zero at S, then in place of Eqs. (85) and (84) we find

$$\delta_2 = A(x + 6.22\lambda_1)^6; \qquad \delta_2 = B(x + 6.22\lambda_1)^{-5} \qquad (155)$$

and the positions of the reflecting planes (cf. Eqs. (87) and (88)) are given by

$$\left. \begin{array}{l} x_3 - x_P = (1/5)(x_P + 6.22\lambda_1), \\ x_P - x_2 = (1/6)(x_P + 6.22\lambda_1). \end{array} \right\} \qquad (156)$$

Thus by Eq. (90) the image force acting on the electrons is

$$F = -(11/4)e^2(x_P + 6.22\lambda_1)^{-2}. \qquad (157)$$

Let us compare these results with those given by the *free path method*. We have seen that for a uniform initial concentration the free path λ_1 is given by Eq. (130). For the non-uniform distribution in the sheath we may thus put

$$\lambda = \lambda_1 \varphi_1{}^{-1/4}, \qquad (158)$$

where φ_1 is given by Eq. (141). We thus find for the Fermi sheath

$$\lambda = (30)^{-1/2}(x + 6.22\lambda_1). \qquad (159)$$

This differs from the expression obtained for the space charge sheath, Eq. (95), only in the value of the two constants. Let us therefore generalize Eq. (159) by putting

$$\lambda = [\alpha(\alpha - 1)]^{-1/2}(x + a), \qquad (160)$$

so that Eqs. (95) and (159) are now special cases corresponding to $\alpha = 2$ and $\alpha = 6$, respectively. Introducing this value of λ in Eq. (94), we find

$$(x_P + a)/(x_3 + a) = (x_2 + a)/(x_P + a) = \exp\{-[\alpha(\alpha - 1)]^{-1/2}\} = 1 - 1/\alpha - 1/24\alpha^3 - 1/48\alpha^4. \qquad (161)$$

To compare this with the result of the exact method, let us see what potential distribution $\varphi_1(x)$ corresponds to the generalized Eq. (160). Eliminating λ from Eqs. (158) and (159) we have

$$\varphi_1 = [\alpha(\alpha - 1)]^2\lambda_1{}^4(x + a)^{-4} \qquad (162)$$

instead of Eq. (141). Substituting this in Eq. (153) and integrating as before, we now find in place of Eq. (155)

$$\delta_2 = A(x + a)^\alpha \quad \text{and} \quad \delta_3 = B(x + a)^{-(\alpha - 1)}. \qquad (163)$$

The method of Eqs. (87) and (88) then gives in place of Eq. (161)

$$(x_P + a)/(x_3 + a) = (x_2 + a)/(x_P + a)$$
$$= 1 - 1/\alpha. \qquad (164)$$

Comparing this with Eq. (161) we conclude that the free path method and the exact method agree whenever we can neglect $(1/24)\alpha^3$ compared to unity. For the case we are considering where $\alpha = 6$ this term is only 0.00019. We find from Eq. (161) that in this case the free path method gives values of $x_3 - x_P$ and $x_P - x_2$, which are greater than those of Eq. (156) by only 0.15 percent and 0.13 percent, respectively.

Case II. $\beta^2 < 0.8$. Since for $x > x_0$ there is no space charge, the potential distribution is represented by the straight line

$$\lambda_1\varphi = -\beta(x - x_0). \qquad (165)$$

Consider now that at some plane P for which $x_P > x_0$ we raise the potential corresponding to

an amount $\delta\varphi$. This changes β by $\delta\beta$ and x_0 by δx_0 so that we have

$$\lambda_1 \delta\varphi = \beta\delta x_0 - (x - x_0)\delta\beta. \qquad (166)$$

By the method used in Eq. (88) we then obtain

$$x_0 - x_2 = -\beta(dx_0/d\beta). \qquad (167)$$

By Eq. (147) this becomes

$$x_0 - x_2 = 1.225\beta^{-1/5}\lambda_1 = (1/5)(x_0 + 6.22\lambda_1). \qquad (168)$$

For small values of β the potential distribution is still approximately a linear function of x for values of x considerably less than x_0. Thus we may apply the *free path method* by substituting the value of φ from Eq. (165) into (158) and the resulting value of λ into Eq. (94). This gives

$$x_0 - x_2 = 1.195\beta^{-1/5}\lambda_1, \qquad (169)$$

which is the same as Eq. (168) except that the constant is 2.5 percent smaller. This good agreement is of interest in view of the fact that the distribution of concentration has a discontinuity at x_0.

Case III. $\beta^2 > 0.8$. At $x = 0$, $\varphi = \varphi_s$ as given by Eq. (138). For $x > 0$, φ is a linear function of x so that

$$\varphi = \varphi_s - \beta x/\lambda_1 = 0.6 - \beta x/\lambda_1 - 0.75\beta^2$$

and $\delta\varphi = -(1.5\beta + x/\lambda_1)\delta\beta$. By the method of Eq. (88), using also Eq. (151), we find

$$x_2 = -1.5\beta\lambda_1 = x_0 - 1.34\lambda_1. \qquad (170)$$

The perturbation method thus locates the reflecting plane at a distance $1.34\lambda_1$ inside of the edge of the displaced Fermi electron gas. The total field $d\varphi/dx$ decreases linearly with x between $x = 0$ and $x = x_0$, but the perturbations continue on through this region of constant positive space charge until they reach displaceable electrons. The potential distribution in this region (values of x slightly less than x_0) is approximately linear (see Fig. 3) and is given by Eq. (165) if β is put equal to 0.894, the value of $\lambda_1 d\varphi/dx$ at x_0. The value of $x_0 - x_2$ given by the free path method is thus obtained by putting $\beta = 0.894$ in Eq. (169) yielding $x_0 - x_2 = 1.23\lambda_1$ which is in rough agreement with Eq. (170).

Effect of image force within the Fermi sheath

In calculating the electron distribution in the Fermi sheath by means of the Poisson equation and the Fermi equation, we have in effect assumed that the pressure gradient in the Fermi electron gas balances at every point the electric force due to the potential gradient resulting from the space charge. The problem we have solved is the one-dimensional analogue of the three-dimensional problem treated by Fermi in his study of the distribution of electrons in atoms.

In both of these treatments, however, the image forces acting on the electrons in the Fermi gas have been neglected. Let us consider the relative magnitudes of the image force and the electric force.

For the case that $\beta = 0$ we find by putting $\varphi_s = 0.6$ in Eq. (137) that the potential gradient at $x = 0$ is

$$(dV/dx_0) = 0.386 V_1/\lambda_1. \qquad (171)$$

The image force on an electron at $x = 0$ can be obtained from Eq. (90) by putting $x_P = 0$. The value of x_3 according to Eq. (156) is $x_3 = 1.245\lambda_1$. The value of $-x_2 = 1.039$ given by Eq. (156) is evidently too small for the electron concentration for $x < 0$ is less than was assumed in the derivation of this equation. Using Eq. (139) for the distribution for $x < 0$ and applying Eqs. (158) and (94) we find by the free path method $x_2 = -1.072$. The image force is thus

$$F = 0.0560e^2/\lambda_1^2.$$

Comparing this with Eq. (171) we find that the ratio of the image force to the force produced by the potential gradient is (see also Eq. (130)) $Fi/F_e = 0.1453e/V_1\lambda_1 = 2.31 V_1^{-3/4}$, where V_1 is in volts. Since V_1 has values that range from 1.5 for caesium to about 19 for tungsten, it appears that the image force in the sheath is by no means negligible but is often greater than the electric force.

The effects of this image force will resemble in many ways that produced by an external field corresponding to values of β comparable with unity (Fig. 3). Thus it compresses the Fermi sheath and gives it a definite outer edge at x_0, for the image force which extends far outside of x_0 prevents any of the Fermi electrons from going more than a definite distance. The electrons in the metal having components of kinetic energy normal to the surface equal to V_1 can thus pass freely to x_0. The work needed to remove electrons from

the metal (Richardson work function at $T=0$) is thus *the work that must be done against the image force in the region outside of* x_0 or is thus equal to the image motive at x_0. The image force within the sheath $(x<x_0)$ is thus of importance only insofar as it is a factor determining the value of x_0 and the magnitude of the image force outside of x_0. The reason that the work done against the image force in removing an electron from the interior of the metal to x_0 is not included in the "work function" is that this force is balanced in this region by the electron pressure and the force due to the potential gradient.

In Part II a method will be developed for calculating the image forces on electrons which lie within the Fermi sheath even when the perturbations produced by an individual electron cannot be considered to be small. This theory will be applied to the forces which hold adsorbed caesium atoms on tungsten surfaces.