(56) for small πckT as follows:

$$\pi ckT/\sin(\pi ckT)=1+\tfrac{1}{6}(\pi ckT)^2+\cdots$$
$$=1+4\pi^2\phi(kT)^2t^2/3F^2+\cdots, \quad (79)$$

where here the argument of t is $F^{\frac{1}{2}}/\phi$. Accordingly the fractional error involved in using the Fowler-Nordheim formula is of the order of $4\pi^2\phi(kT)^2/3F^2$. This is in agreement with the results of Sommerfeld and Bethe[5] and Guth and Mullin, their Eq. (12)[6]; only the numerical factors differ slightly.

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Theory of the Sputtering Process*

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The mathematical methods of neutron diffusion theory are applied to the problem of cathode sputtering. The state of all particles not in thermal equilibrium with the lattice can be described by a gas-like model in which the atoms move with constant mean free path. Collisions are assumed to occur only with "fixed" lattice atoms, but binding energies are neglected. The distribution functions exhibit finite discontinuities in the energy which approximate the behavior of the correct functions. The sputtering ratio is determined by integration over the velocity direction and also over energy, thus averaging out the approximation. The resulting expression for the sputtering ratio depends upon four atomic parameters of the system. In principle all are measurable, but only the mass ratio is known with precision at the present time. The theoretical curve is fitted to the experimental data which are available for eight ion-metal combinations. The curve is found to be very sensitive to the choice of fitting parameters, and the parameters exhibit considerable internal consistency. The theory indicates certain areas of experimental research which should add to present understanding of the process.

I. INTRODUCTION

DISINTEGRATION of cathodes by positive-ion bombardment has been under discussion in the literature for slightly more than 100 years.[1] Glockler and Lind[2] summarize the information available in 1939. A more modern survey, including a critical study of the theoretical work, is given by Massey and Burhop.[3]

The theory proposed in this article is a logical development of the ideas of Kingdon and Langmuir,[4] but conceptually it lies between their approach and the completely thermal method of Townes.[5] Mathematically it closely resembles the methods developed to study the diffusion of neutrons in solids.[6]

The sputtering process was analyzed as follows: a beam of ions strikes a metallic surface and dislodges atoms. The actual process probably involves the penetration of the ions into the surface, where they "cool" into thermal equilibrium with the lattice by making collisions with the lattice atoms. These "struck" particles acquire an appreciable energy which must be dissipated by collisions with particles which are still bound in lattice sites. Thus the steady state consists of two distributions of moving atoms, one describing the state of all incident atoms and the other the state of all "struck" atoms, which interact with the stationary distribution of lattice particles. If the corresponding distribution functions can be calculated, the sputtering ratio, the number of atoms sputtered per incident ion, is determined by the flux of "sputtered" lattice atoms through the surface.

We assume that the distribution functions are solutions of the Boltzmann integro-differential equation written in the form known as the transport equation. Thus we are accepting all of the assumptions inherent in that formulation. The validity of this assumption will be discussed later in greater detail.

II. DISTRIBUTION FUNCTIONS

It is convenient to describe the process as the interaction of four distributions, where each of those previously mentioned is split into two parts. This method allows the interesting portions of the distributions to be represented by functions which are approximately isotropic.

The first distribution, hereafter known as the "beam," shall consist of those particles which have penetrated into the lattice without having made a collision. These particles are within the metal, but they are still moving in their initial direction with their original energy. For convenience this incident beam will be considered mono-

* Portions of this work were submitted to the faculty of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] W. R. Grove, Trans. Roy. Soc. (London) **142**, 87 (1852).

[2] G. Glockler and S. Lind, *The Electrochemistry of Gases and other Dielectrics* (John Wiley and Sons, Inc., New York, 1939), Chap. XIX.

[3] H. Massey and E. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), pp. 578–594.

[4] K. Kingdon and I. Langmuir, Phys. Rev. **22**, 148 (1923).

[5] C. Townes, Phys. Rev. **65**, 319 (1934).

[6] See, for example, R. Marshak, Revs. Modern Phys. **19**, 185 (1947).

energetic, with all particles moving in the positive z direction. Here z will be in the direction of the inward drawn normal of an infinite plane metal surface.

The second distribution, the "incident particle" distribution, consists of those beam particles which have made one or more collisions without having "cooled" into thermal equilibrium with the lattice.

The third distribution, the "lattice particle" distribution, includes those lattice particles which are not in thermal equilibrium with the lattice, i.e., those lattice-type particles which have just been struck and therefore have not had time to "cool."

The fourth, the "metal," contains all particles, incident and lattice, which are in thermal equilibrium with the lattice as a whole. The density of the former will be assumed negligible compared to the latter. We shall assume that this distribution is "smeared out" into a uniform density of material, designated by ρ. Actually we are assuming that the mean free paths, or collision probabilities, are functions of velocity and not of position. This use of ensemble average or effective values is a mathematical artifice to facilitate calculations and has not been justified physically. The same procedure seems to be effective in neutron transport calculations performed to this degree of precision.

Defined in this way, the first distribution function will depend only upon the penetration, z, while the next two depend upon penetration and velocity. Preliminary calculations using reasonable beam densities indicate that collisions between two moving particles may be neglected.

When the "target" distribution can be written in this smeared-out form, the Boltzmann equation becomes the transport equation. The distribution functions, which satisfy this equation with the symmetry previously described, must be symmetric in velocity direction about the z axis; so that only two parameters are needed to specify the velocity. Instead of the usual components we shall use the logarithmic energy, $u=\ln(E_0/E)$ (where E is the energy of a particle and E_0 is the energy of a beam particle before collision), and p, the direction cosine of the particle velocity with respect to the z axis. In terms of these variables, the transport equation takes the form[6]

$$\frac{P}{\eta(u)}\frac{\partial L}{\partial z}=-L+\int dp'\int du'L(u',z,p')\times f(u',u,p_0)h(u')+W(u,z,p), \quad (1)$$

where $\eta(u)=\rho\sigma$ is the reciprocal of the mean free path of a moving particle within the metal. Here σ is the total cross section of the moving particles upon the lattice atoms; so that η is the macroscopic cross section.

The function L is defined as $L(u,z,p)=N(u,z,p)\times v\eta(u)$, where $N(u,z,p)$ is the required distribution function and v is the velocity under consideration. Note that if L, the collision frequency per unit volume, is known, then N, the distribution function, is completely determined.

The function $f(u',u,p_0)$ is the probability that a particle initially in a logarithmic energy state u' will be in a logarithmic energy state u after a collision. Here p_0 defines the scattering angle. In the rest of the work this function will be referred to as the *direct* energy transition function.

The remaining factor under the integral is defined by the relation

$$h(u')=\sigma_s(u')/[\sigma_s(u')+\sigma_t(u')], \quad (2)$$

where σ_s is the cross section for scattering, and σ_t is the cross section for trapping by the lattice. (Note that σ_t corresponds to the cross section for capture in the neutron diffusion literature.) We shall refer to $h(u')$ as the *trapping parameter.*

We assume that a trapped atom is brought into thermal equilibrium with the lattice as the result of a single collision. In general a moving atom will make several collisions which reduce its energy to the point that it can be trapped. Thus although σ_s and σ_t are functions of the energy, we expect most of the energy variation of σ to come from σ_t which will increase rapidly as the energy decreases. If this is true, σ_t increases with increasing logarithmic energy, and h decreases.

If σ_s and σ_t were known functions of the energy any difficulties would be entirely mathematical. Unfortunately we have no quantitative information about their behavior; so the treatment of cross sections becomes one of the weakest parts in the entire development. The problem will be formulated on the assumption that these functions are known, but for comparison with experiment they are assumed constant; so that h and η_m can be used as fitting parameters. For systems on which data are available, this constant value assumption appears to be valid so long as the mass ratio is greater than 0.1. Fitting is possible for smaller mass ratios, but the data are scattered and the results suspicious. Apparently h is much more energy-sensitive than the η_m.

Finally, $W_m(u,z,p)$ is $1/2\pi$ times the source strength of particles for the particular distribution.

Beam

The only source of particles for the beam distribution is the flux of ions through the metal's surface. We shall assume that the ions are immediately neutralized upon entering the metal so that electrical forces may be neglected. The beam distribution is so designed that any collision removes the particle from the distribution, and hence the rearrangement (integral) term of the transport equation must vanish. The resulting equation may be solved immediately if we assume that the mean free path is not a function of the energy, and it follows that

$$N_0=N_e e^{-\eta_i z}, \quad (3)$$

where $N_e/2\pi$ is the density per cubic centimeter of the incident flux. The exponential form of this distribution function greatly simplifies the determination of the incident particle distribution function.

Metal

The energy at which a particle becomes a member of the metal distribution will be left unspecified. Consideration of the requirements of conservation of energy and of particles shows that it could be determined if the distribution functions were accurately known, but the process would be extremely complicated. In practice, no attempt has been made to evaluate this energy, because we find that the lower limit of the energy range can be determined in another way.

Throughout the work, we are assuming that the number of moving particles is negligible compared to the number of metal particles. Because collisions between two moving particles may be neglected, all collisions are "cooling" collisions; that is, the energy of the moving particle is decreased.

Fundamental Equations

Now that the first distribution function has been relegated to the role of source term for the second, and the fourth has been merged with the bulk cross section, we can concentrate our attention upon the incident particle and lattice particle distributions. The subscript i will refer to the incident type of particle and its distribution function and j will refer to the lattice-type particles and their distribution function. The subscript m refers to either type of moving particle.

The beam distribution function determines the source strength for the incident particle distribution, because any particle introduced into this distribution must come from the beam. That is dN_0/dz must be proportional to the required source strength. This rate, multiplied by the appropriate f function will give the probability that a particle will be introduced with a particular value of u and p. Thus

$$W_i \equiv N_e \eta_i v_0 e^{-\eta_i z} f_i(0,u,p) = N e^{-\eta_i z} f_i(0,u,p), \quad (4)$$

and the transport equation for the incident particle distribution function may be written

$$\frac{p}{\eta_i(u)} \frac{d}{dz}(L_i) = -L_i + \int dp' \int du' L_i f_i h_i + W_i. \quad \text{(I)}$$

This equation will be called the first fundamental equation.

To determine the second fundamental equation we must define a new energy transition probability function. Let $F_m(u',u,p_0)$ be the probability that a particle of logarithmic energy u' will transfer a logarithmic energy u to the struck particle, sending it in the p_0 direction. Obviously this function is related to $f_m(u',u,p_0)$ and can be evaluated by similar techniques.

The source strength for the lattice distribution can now be written as the sum of three terms corresponding to three orders of approximation to the distribution function. Thus

$$W_{j0} \equiv N_e \eta_i v_0 e^{-\eta_i z} F_i(0,u,p) = N e^{-\eta_i z} F_i(0,u,p) \quad (5)$$

represents the production by collisions of "beam" particles with metal atoms, while

$$W_{j1} \equiv \int dp' \int du' L_i(u',z,p') F_i(u',u,p_0) \quad (6)$$

is the production by collisions of "incident" particles with the metal, and

$$W_{j2} \equiv \int dp' \int du' L_j(u',z,p') F_j(u',u,p_0) \quad (7)$$

is the production by moving lattice atoms. We shall expect the contributions of the second and third terms to increase as the energy of the beam particles is increased. Then, if $W_j = \sum_n W_{jn}$, the second fundamental equation takes the form

$$\frac{p}{\eta_j(u)} \frac{d}{dz}(L_j) = -L_j + \int dp' \int du' L_j f_j h_j + W_j. \quad \text{(II)}$$

Note that this separation of source terms is possible only if collisions between two moving particles can be neglected. If this assumption is not made, the two fundamental equations must be solved simultaneously. In the present formulation the first may be solved independently, and this solution provides part of the complete solution to the second.

Energy Transition Functions

If we assume hard-sphere collisions, which appears reasonable because of the energies involved in the usual sputtering experiments, the energy transition functions can be evaluated immediately. The direct function, f_m, has been discussed in the literature[6] and its derivation need not be repeated here. The *indirect* function, F_m, is evaluated from the same formulation of the collision kinetics with attention focused upon the struck particle after the collision. The functions and related quantities are defined in Table I. The quantity μ is the mass ratio, $\mu = M_i/M_j$.

In this formulation we neglect the binding energy of the struck particles. This assumption is probably valid for kev incident particle energies, but is questionable near the sputtering threshold. The low-energy portions of the theoretical curves are probably less reliable, and the threshold values may be considerably in error for this reason. The available data do not justify generalizing these functions which would greatly increase the mathematical difficulties of the theory.

We find that there is a maximum logarithmic energy loss, ϵ_m, possible in a single collision. Similarly there is a

TABLE I. Definitions and properties of the energy transition functions, including the complete and approximate Laplace transforms of the functions.

$$f_m=(a_m/2\pi)e^{-(u-u')}\delta[p_0-\vartheta(u-u')]\ ;\quad 0\leqslant u-u'\leqslant\epsilon_m$$
$$=0\ ;\quad \epsilon_m<u-u'\leqslant\infty$$
$$F_m=(a_m/2\pi)e^{-(u-u')}\delta[p_0-\Theta(u-u')];\quad \nu_m\leqslant u-u'\leqslant\infty$$
$$=0\ ;\quad 0\leqslant u-u'<\nu_m$$

$$\vartheta_m=b_m\exp[-(u-u')/2]-c_m\exp[+(u-u')/2],$$
$$\Theta_m=a_m^{\frac{1}{2}}\exp[-(u-u')/2],$$
$$a_m=(1+\mu)^2/4\mu,$$
$$b_m=(1+\mu)/2\mu,$$
$$c_m=(1-\mu)/2\mu.$$

Letting $(s+1)=v$,

$$\bar{f}_{m0}=[a_m/v][1-e^{-v\epsilon_m}],$$
$$\bar{f}_{m1}=a_m\{[b_m/(v+\tfrac{1}{2})][1-e^{-(v+\frac{1}{2})\epsilon_m}]-[c_m/(v-\tfrac{1}{2})][1-e^{-(v-\frac{1}{2})\epsilon_m}]\},$$
$$\bar{F}_{m0}=(a_m/v)e^{-v\nu_m},$$
$$\bar{F}_{m1}=[a_m^{\frac{1}{2}}/(v+\tfrac{1}{2})]e^{-(v+\frac{1}{2})\nu_m}.$$

In the p_{Av} approximation, these reduce to the following:

$$\bar{f}_{i0}=(a_i/v)E_1(v),$$
$$\bar{f}_{i1}=(\tfrac{2}{3})(\mu a_i/v)E_1(v),$$
$$\bar{F}_{j0}=(a_i/v)E_2(v),$$
$$\bar{F}_{j1}=(\tfrac{2}{3})(\mu a_i/v)E_2(v),$$

where

$$E_1(v)=(1-e^{-v\epsilon_i}),$$
$$E_2(v)=e^{-v\epsilon_i}.$$

minimum logarithmic energy, ν_m, which the struck particle may acquire. Note that these logarithmic energies are not numerically equal, although they have the *same* reference energy.

The discontinuous form of both f_m and F_m will simplify our evaluation of the integral terms of the transport equation. The energy transition functions also determine the limits of integration in the rearrangement term. Thus for direct transitions $(u-\epsilon_m)\leqslant u'\leqslant u$, while for indirect $0\leqslant u'\leqslant(u-\nu_m)$. In both cases $-1\leqslant p'\leqslant 1$.

III. FIRST FUNDAMENTAL EQUATION

The initial step in our determination of L_i will be to simplify the angular dependence of the first fundamental equation. As the distribution function, source strength, and energy transition function are all approximately spherically symmetrical, we begin by expanding all three of these functions in a series of Legendre polynomials of p. All of the functions take the form

$$X(p)=\left(\frac{1}{4\pi}\right)\sum_{n=0}^{n=\infty}(2n+1)P_n(p)X_n,$$

where

$$X_n\equiv 2\pi\int_{-1}^{1}dpP_n(p)X(p).$$

When the expanded forms are substituted into Eq. (I) and the usual procedure of multiplication by $P_n(p)$ and integration over p is followed, we obtain the set of equations

$$\left[\frac{1}{\eta_i(u)}\right]\frac{dL_{i1}}{dz}=-L_{i0}+\int_0^u du'L_{i0}f_{i0}h_i+W_{i0},$$

$$\frac{1}{\eta_i(u)}\left[\frac{n}{2n+1}\frac{dL_{i\,n-1}}{dz}+\frac{n+1}{2n+1}\frac{dL_{i\,n+1}}{dz}\right]$$
$$=-L_{in}+\int_0^u du'L_{in}f_{in}h_i+W_{in};\quad n\geqslant 1.$$

Here the integration extends from 0 to u because of the step function nature of f_i and hence of the f_{in}.

Now assume that h_i can be removed from under the integral sign of these equations. This can be interpreted in two ways: either the cross sections for scattering and trapping are not functions of the energy, as discussed above; or we are defining h_i as a weighted average of the correct trapping parameter over the range of energy under consideration. Our detailed knowledge of the process is very limited, but the latter assumption seems most reasonable.

Our next step is to define the Laplace transform of the functions

$$T[X_{in}(u)]\equiv\bar{X}_{in}(s)\equiv\int_0^\infty e^{-us}X_{in}(u)du,\qquad(8)$$

where

$$T[L_{in}/\eta_i(u)]\equiv\bar{\lambda}_{in},$$

and then write the set of equations in terms of the transformed quantities. The integral terms cause no difficulty because they are convolution integrals. We obtain

$$\frac{d\bar{\lambda}_{i1}}{dz}=-\gamma_{i0}(s)\bar{L}_{i0}(s,z)+\bar{W}_{i0}(s,z),$$

$$\frac{1}{(2n+1)}\left[n\frac{d\bar{\lambda}_{i\,n-1}}{dz}+(n+1)\frac{d\bar{\lambda}_{i\,n+1}}{dz}\right]$$
$$=-\gamma_{in}(s)\bar{L}_{in}(s,z)+\bar{W}_{in}(s,z);\quad n\geqslant 1$$

here

$$\gamma_{in}(s)\equiv(1-h_if_{in}(s)).\qquad(9)$$

As the distribution function is approximately isotropic, the $\bar{L}_{i2}$ and higher order terms will be neglected, and the set of equations reduces to the following pair:

$$d\bar{\lambda}_{i1}/dz=-\gamma_{i0}\bar{L}_{i0}+\bar{W}_{i0},$$
$$\tfrac{1}{3}d\bar{\lambda}_{i0}/dz=-\gamma_{i1}\bar{L}_{i1}+\bar{W}_{i1}.$$

These equations correspond to a diffusion approximation for the dependence on the space variable, z.

Now our problem is to obtain the simultaneous solution of these two equations with appropriate boundary conditions. One further analytic simplification is desirable. The functional form of the $\eta_m(u)$ is not known; so it is convenient to assume that $\eta_i(u)=\eta_i=$ const.

This assumption is quite reasonable because the mean free path probably depends more strongly upon the lattice spacing and particle diameter than upon the energy. The equations then become

$$\frac{1}{\eta_i}\frac{d}{dz}\bar{L}_{i1}=-\gamma_{i0}\bar{L}_{i0}+\bar{W}_{i0},$$

$$\frac{1}{3\eta_i}\frac{d}{dz}\bar{L}_{i0}=-\gamma_{i1}\bar{L}_{i1}+\bar{W}_{i1}.$$

We now recall that $W_{in}(u,z)$ can be written in the form $W_{in}(u,z)=W_{in}(u,0)\exp(-\eta_i z)$; so that the transform operator affects only the first factor, giving $\bar{W}_{in}(s,z)=\bar{W}_{in}(s,0)\exp(-\eta_i z)$.

It is now possible to eliminate $\bar{L}_{i1}$ between these two equations, with the following result:

$$d^2\bar{L}_{i0}(s,z)/dz^2=\omega_i^2(s)\bar{L}_{i0}(s,z)+K_0(s)e^{-\eta_i z}, \quad (11)$$

where

$$\begin{aligned}&\omega_i^2(s)\equiv 3\eta_i^2\gamma_{i0}\gamma_{i1},\\ &K_0(s)\equiv -3\eta_i^2[\bar{W}_{i0}(s,0)\gamma_{i1}+\bar{W}_{i1}(s,0)].\end{aligned} \quad (12)$$

It is interesting to note that when we restrict Eq. (11) with a requirement $s^2\ll 1$ and make a linear change of variable in transform space, it reduces to the "age equation." This method has certain mathematical similarities to an age approximation, but it is valid over a wider energy range.

An examination of the rate at which the separate components of the distribution function are changing suggests

$$\lim_{z\to\infty}\bar{L}_{i0}(s,z)=0, \quad \lim_{z\to 0}\frac{d}{dz}[\bar{L}_{i0}(s,z)]=\bar{W}_{i1}(s,0),$$

as boundary conditions for Eq. (11). The first condition is quite standard, but the second requires some comment. Basically it says that the distribution function is space-symmetric at $z=0$ except for the source-term contribution. This term, which was neglected in the numerical calculations, introduces a surface scattering effect into the distribution. Its contribution is at least an order of magnitude less than the other terms in the distribution function.

These conditions are sufficient to determine the solution of Eq. (11) as

$$\bar{L}_{i0}(s,z)=\bar{A}(s)e^{-\omega_i(s)z}+\bar{B}(s)e^{-\eta_i z}, \quad (13)$$

where the amplitudes, functions of s only, are

$$\begin{aligned}&\bar{A}(s)\equiv -[\eta_i/\omega_i(s)][3\bar{W}_{i1}(s,0)+\bar{B}(s)],\\ &\bar{B}(s)\equiv K_0(s)/[\eta_i^2-\omega_i^2(s)].\end{aligned} \quad (14)$$

We need not carry our analysis of the first fundamental equation beyond this point, as the remaining development depends only upon the Laplace transform of the incident particle collision frequency.

Marshak[6] and Placzek[7] have discussed functions which are similar to L_{i0}, but the present formulation is more useful for this particular problem.

IV. SECOND FUNDAMENTAL EQUATION

Formally, there is no difference between the first and second fundamental equations except that in this case the source consists of three terms. The procedure described above is followed, and the solution takes the same general form. After taking the Laplace transform, we note that the third source term may be combined with the rearrangement term. Thus we write

$$\Gamma_n\equiv 1-h_j\bar{f}_{jn}-\bar{F}_{jn}. \quad (15)$$

In terms of the Γ_n, Eq. (II) becomes

$$\frac{1}{\eta_j}\frac{d\bar{L}_{j1}}{dz}=-\Gamma_0\bar{L}_{j0}+\bar{W}_{j0},$$

$$\frac{1}{3\eta_j}\frac{d\bar{L}_{j0}}{dz}=-\Gamma_1\bar{L}_{j1}+\bar{W}_{j1},$$

and again eliminating between these two equations,

$$d^2\bar{L}_{j0}/dz^2=\omega_j^2(s)\bar{L}_{j0}(s,z)+K_1(s)e^{-\eta_i z}+K_2(s)e^{-\omega_i(s)z},$$

where

$$\begin{aligned}&\omega_j^2(s)\equiv 3\eta_j^2\Gamma_0\Gamma_1,\\ &K_1(s)\equiv -3\eta_j^2[(N+\bar{B}(s))\bar{F}_{i0}\Gamma_1\\ &\qquad +(\eta_i/\eta_j)(N+\bar{B}(s)\gamma_{i0})\bar{F}_{i1}],\\ &K_2(s)\equiv -3\eta_j^2[\bar{F}_{i0}\Gamma_1+(\eta_i/\eta_j)\bar{F}_{i1}\gamma_{i0}][\bar{A}(s)-\bar{B}(s)].\end{aligned} \quad (16)$$

The functions $\bar{A}(s)$ and $\bar{B}(s)$ are defined in Sec. III. As before, barred symbols, functions of s, refer to the Laplace transform of the corresponding function. When the differential equation is assumed to have a solution of form of Eq. (13), and the same boundary conditions are applied, we find

$$\bar{L}_{j0}(s,z)=\bar{D}(s)e^{-\omega_j(s)z}+\frac{K_1(s)}{\eta_i^2-\omega_j^2(s)}e^{-\eta_i z}+\frac{K_2(s)}{\omega_i^2(s)-\omega_j^2(s)}e^{-\omega_i(s)z}, \quad (17)$$

where

$$\bar{D}(s)\equiv -\left(\frac{\eta_j}{\omega_j(s)}\right)\bar{W}_{j0}-\frac{\eta_i K_1(s)}{\omega_j(s)[\eta_i^2-\omega_j^2(s)]}-\frac{\omega_i K_2(s)}{\omega_j(s)[\omega_i^2(s)-\omega_j^2(s)]}. \quad (18)$$

We now begin the final step, the calculation of the inverse transformation (inversion) of the function $\bar{L}_{j0}(s,0)$.

[7] G. Placzek, Phys. Rev. 69, 423 (1946).

V. INVERSE TRANSFORMATION

The inversion process is considerably simplified if we now make the following physical approximation. We let $f_{i1}(u)=\frac{2}{3}\mu f_{i0}(u)$ which is equivalent to replacing p by p_{Av} in the definition of $f_{i1}(u)$. It is apparent that this is a satisfactory approximation for small μ. Later we will discuss the meaning of this approximation in more detail.

Even with this approximation, $\bar{L}_{j0}(s,z)$ is an extremely complicated function of s. In such cases it is most convenient to consider the inversion of separate factors and then use the convolution theorem to obtain the inversion of the complete function.

The most difficult factors are those of the form $\exp[-g(s)z]$; so we consider them first. It has been shown by Widder[8] that the following theorem holds: If $\bar{f}(s)=T[f(t)]$, then it can be shown that

$$\lim_{k\to\infty}\frac{(-1)^k}{k!}\binom{k}{-t}^{k+1}\bar{f}^{(k)}\binom{k}{-t}=f(t),$$

where $\bar{f}^{(k)}$ is the kth derivative of the function with respect to its argument. The mathematical conditions on the theorem are not restrictive for physical problems.

Applying this theorem to a function of the form $\exp[-g(s)z]$, we see that its Laplace inversion must vanish at $z=0$. Thus if we make the additional physical approximation that, because of the small mean free path, a particle must actually make a collision at the surface to escape, our expression for $\bar{L}_{j0}(s,z)$ reduces to

$$\bar{L}_{j0}(s,0)=K_1(s)/[\eta_i^2-\omega_j^2(s)], \tag{19}$$

which can be handled by normal techniques. We note that this function is a first approximation to the correct collision frequency, even if the mean free path assumption is not reasonable.

After some tedious algebra in which it is convenient to set $(s+1)=v$, we find

$$\bar{L}_{j0}(v,0)=R(v)[(e_1v-e_2)\{N+\bar{B}(v)\}-e_3\bar{B}(v)E_1(v)]E_2(v), \tag{20}$$

where

$$R(v)=e_4/(v-r_1)(v-r_2),$$
$$\bar{B}(v)=\tfrac{1}{2}(N/v^2)(e_5-e_6v)[v-e_7E_1(v)]^{-1}E_1(v),$$
$$E_1(v)=1-e^{-\epsilon_i v},$$
$$E_2(v)=e^{-\nu_i v},$$

and the e_n and r_n are constants which depend upon the parameters $\mu,\eta=\eta_i/\eta_j$, and $h=h_i=h_j$.

The factor $\{v-e_7[1-\exp(-\epsilon_i v)]\}^{-1}$ which appears in $\bar{B}(v)$ is of considerable physical as well as mathematical interest. It is a particularly complicated form of the "jump function" which is used in the solution of difference equations.[9] This factor modifies $\bar{B}(v)$ so that its inverse function appears as a discontinuous function of the energy, where both positive and negative values are possible, convoluted by a decaying exponential function of the energy. The resulting function has alternating positive and negative steps whose amplitude decreases exponentially, $B(u)$ always remaining positive. The actual inversion to real space is accomplished by expansion in v and termwise inversion. Fortunately the real space exponential decays rapidly; so that only three terms of the expansion must be retained. The number of terms required depends upon the mass ratio through ϵ_i which controls the separation between steps on the energy scale.

We expect this behavior with a source function which was initially postulated as discontinuous. Computational difficulties are increased because the collision frequency is represented by different functions in certain regions of the energy variable, but our understanding of the problem is not affected.

We can now interpret the p_{Av} approximation which was made earlier in the work. Removal of this approximation increases the complexity of the "jump factor" and introduces more fine structure into the distribution function. As we are interested in the *integrated* distribution function the approximation seems reasonable until the experimental curves are available to a higher degree of precision.

The factor $E_2(v)$ which was introduced from $\bar{F}_{i0}$, and also from $\bar{F}_{i1}$ in the p_{Av} approximation, has an interesting physical significance. We recall that ν_m was associated with the maximum energy which could be transferred in a collision. This energy must be equal to or greater than the threshold energy for the process to be possible. Therefore we may take as the limiting case $\nu_m=\ln(E_0/E_t)$; so that $(u-\nu_m)=\ln(E_t/E)$, which appears in the inversion process from the $E_2(v)$ factor, is just the logarithmic energy referred to the threshold energy rather than the beam energy. With u written in terms of this reference the algebra is much simpler.

It is now a straightforward if somewhat involved process to obtain the inversion of $\bar{L}_{j0}(s,0)$ as defined by Eq. (19). The results appear as a sum of three terms whose complexity depends upon the number of terms carried in the jump function. Once the collision frequency is known it is not difficult to calculate the flux of metal particles through the surface by integrating over the possible angles of emission.

VI. SPUTTERING RATIO

The sputtering ratio is now obtained by integrating the metal atom flux over the allowable values of the logarithmic energy, $0\leqslant u\leqslant u'$, which correspond to the energy range $E_0\leqslant E\leqslant E_t$. The resulting expression for the sputtering ratio takes the form

$$R(u')=\sum_{n=1}^{n=3}S_n(e^{r_nu'}-1), \tag{21}$$

[8] D. V. Widder, *The Laplace Transform* (Princeton University Press, Princeton, 1946), pp. 288 ff. There is a misprint in the initial statement of the theorem.

[9] W. Thomson, *Laplace Transformation* (Prentice-Hall, Inc., New York, 1950).

where the S_n have different values in the ranges $0 \leqslant u' \leqslant \epsilon_i$; $\epsilon_i \leqslant u' \leqslant 2\epsilon_i$; $2\epsilon_i \leqslant u' \leqslant 3\epsilon_i$; etc. The algebraic forms of the constants S_n and r_n are very complicated, and will not be reproduced here.

The final function, $R(u')$, depends upon the following parameters of the physical system: $\mu = M_i/M_j$, the mass ratio, h, the trapping parameter, $\eta = \eta_i/\eta_j$, the mean free path ratio, and finally E_t, the threshold energy.

In principle, all of these parameters should be experimentally measureable; however, of the four, only μ is accurately known. Of the others, we can make some educated guesses about the order of magnitude of E_t, and h and η are completely unknown.

The constants are very complicated functions of the parameters, but a few generalizations are possible. Thus the r_n are extremely sensitive to h, and are very insensitive to η. The S_n vary directly with η, and are relatively unaffected by h. Neither the S_n nor the r_n

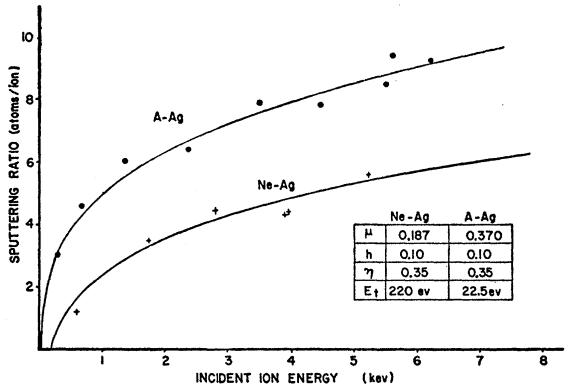

FIG. 1. Comparison of theory and experiment for A—Ag and Ne—Ag. The 300-ev point of the A—Ag curve appears in Keywell's original letter, but was inadvertently omitted in the long paper. In a private communication Dr. Keywell has suggested that all of his experimental points may be uncertain by as much as 15% of the sputtering ratio.

depend upon E_t. Approximately, h controls the shape of the sputtering ratio curve, and η its magnitude.

VII. COMPARISON WITH EXPERIMENT

Probably the most reliable total sputtering ratio curves are those of Keywell.[10] The experimental method which he has described appears to be the most satisfactory so far devised for this type of measurement; the only apparent difficulty being that the amount of bombarding material trapped in the target was not determined, although it may affect the weight of the target after bombardment.

To compare with experiment we plot R as a function of E_0; the actual fitting was done by trial and error, but is very sensitive to the values chosen for the parameters. Thus if any parameter is varied by 10%

[10] F. Keywell, Phys. Rev. **87**, 160 (1952); **97**, 1611 (1955). The author would like to thank Dr. Keywell for the use of his data in advance of publication.

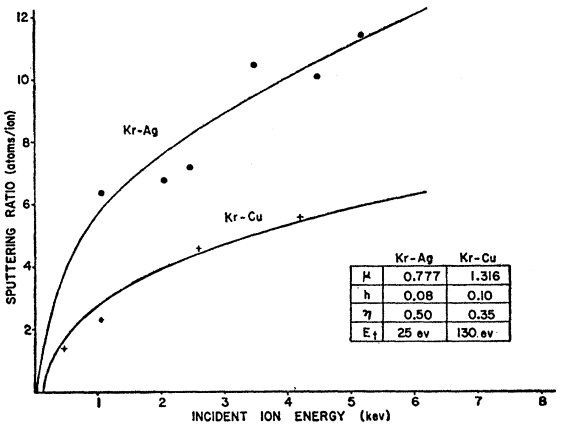

FIG. 2. Comparison of theory and experiment for Kr—Ag and Kr—Cu. The Kr—Ag curve appears to be significant because it contains a reasonable number of points, but the low-energy end is questionable. The Kr—Cu system is included only because the parameters are in line with those for several other systems. The data are much too incomplete to insure that this is the correct fit.

of its value the curve is noticeably changed. Furthermore, the curve *cannot* be readjusted by variation of the other parameters.

The results for six cases are shown in Figs. 1, 2, and 3. This theory appears adequate for these mass ratios, and there are regularities in the parameters for similar atomic systems; see Table II. The threshold for Kr-Cu is not out of line with the general trend, because here the mass ratio is greater than unity. The minimum logarithmic energy transferrable, ν_i, begins to increase when $\mu > 1$. This behavior is to be expected from the conservation of momentum requirement in a single collision.

In Fig. 4 we see the best single-parameter fits of the theory and experimental data for two systems of small mass ratio. Here the theory is not as satisfactory, but the behavior of the curves suggests the following explanation: a single choice of the parameter h is not satisfactory over the entire experimental range. Thus the averaged value of h, which we assumed in the de-

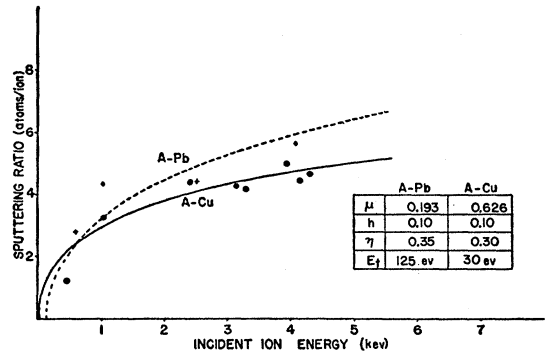

FIG. 3. Comparison of theory and experiment for A—Pb and A—Cu. The A—Pb curve is probably not significant, but is included because again the parameters fit the pattern. Next to the A—Ag pair, the A—Cu is probably the most useful system. Unfortunately it does not extend into the higher energy range.

TABLE II. Comparison of the parameters for the eight available atomic systems. μ is the mass ratio, h the trapping parameter, η the macroscopic cross-section or mean-free-path ratio, and E_t the sputtering threshold energy. Notice the general trend of decrease of E_t with increasing mass ratio for $\mu<1$, and the considerable internal consistency of the other parameters for similar systems.

System	μ	h	η	E_t(ev)
He–Pb	0.0193	0.04	0.04	275
He–Ag	0.0371	0.30	0.05	250
Ne–Ag	0.187	0.10	0.35	220
A–Pb	0.193	0.10	0.35	125
A–Ag	0.370	0.10	0.35	22.5
A–Cu	0.626	0.10	0.35	30
Kr–Ag	0.777	0.08	0.50	25
Kr–Cu	1.316	0.10	0.35	130

velopment, is not sufficient in the case of small mass ratios. This agrees with the results of neutron cooling experiments. If h is a function of the energy, we are not allowed to remove it from under the integral sign in the transport equation, and the theory is much more complicated. It would be very difficult to extend the theory in this direction unless h is a known function of u.

No attempt has been made to fit Keywell's data for the sputtering of silver by hydrogen. The diatomic nature of the ion, and the resulting possibility of fragmentation in a collision, forces a reexamination of the collision mechanics for this single case, which hardly seems worthwhile at this time.

When more work has been done on the threshold energy values it may be possible to relate E_t to the atomic heat of vaporization through the hard sphere maximum energy transfer relation. It is probable that the threshold for normal incidence will be different from that for fine wires. The incident particles arriving with low energy, but almost parallel to the surface, could very well remove a lattice atom by means of a "plowing" effect across the surface. Experimental work along these lines has been carried out by Fetz[11] and Wehner.[12]

VIII. ANALYSIS AND CONCLUSIONS

In conclusion, we should take a closer look at some of the basic assumptions made in this work. For example, the assumption that the distribution functions must satisfy the transport equation is not justified, because in all probability the binary collision requirement, made in the development of that equation, is not met in the problem under consideration. In addition, the entire process takes place in a very thin region near the surface of the metal, or the particles would lose their energy before they could escape. This makes the assumption $\eta \neq \eta(z)$ quite questionable.

Fortunately the surface roughness of the metal tends to overcome the last difficulty. In the development this surface is assumed to be a mathematical plane which levels the surface, i.e., which leaves as many vacant sites within the surface as there are atoms outside, but the actual irregularities may be greater than the mean depth of penetration from which particles ultimately escape. At worst, the distributions obtained in this manner must be first approximations to the correct distribution functions.

The theory provides a semiquantitative explanation of the sputtering mechanism. Unfortunately it depends upon unknown atomic parameters, but it has the advantage over other theories that the parameters are relatively few in number, and that they should be at least approximately measurable. When these measurements have been made, significant improvements should be possible. Until this has been done, a further compounding of approximations hardly seems justified.

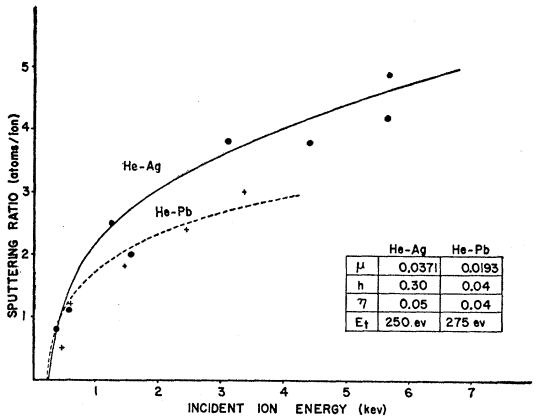

FIG. 4. Comparison of theory and experiment for He–Ag and He–Pb. Note the change of scale. The He–Ag system is quite complete, but the He–Pb is very questionable. The fitting is not so satisfactory as for systems of higher mass ratio.

ACKNOWLEDGMENTS

The author would like to express his indebtedness to Professor Henry Margenau, who suggested the problem and guided the preliminary work, to Professor R. L. Gluckstern and Dr. W. R. Heller for many hours spent in discussion of its manifold ramifications, and finally to Miss Betty Custis and Miss Geraldine Thielmeier, his students at the University of Louisville, who carried out the computations.

[11] H. Fetz, Z. Physik. **119**, 590 (1942).
[12] G. Wehner, Phys. Rev. **93**, 633 (1954).