A Test of the Classical "Momentum Transfer" Theory of Accommodation Coefficients of Ions at Cathodes

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On the classical theory of momentum transfer at impact of a moving particle with a stationary particle, one of us suggested that the accommodation coefficient for positive gas ions striking a metal cathode should be less than unity only if the mass of the metal atom exceeds that of the gas ion. To test this hypothesis, momentum experiments of the type already reported for helium ions striking a molybdenum cathode have been continued for argon ions striking molybdenum and aluminum, respectively. The transfer of momentum was measured by the deflection of a delicate pendulum, whose bob consisted of the metal cathode under investigation, the surrounding argon atmosphere being strongly ionized by a discharge between supplementary electrons. The experimental data made possible the computation of the accommodation coefficient for the positive ions and also the fraction of the current carried by electrons at the cathode. The accommodation coefficient for argon ions on molybdenum was 0.8, in good agreement with the value obtained by Compton and Van Voorhis by thermal measurements, while for argon ions on aluminum the accommodation coefficient was unity, in accordance with the above prediction. The classical theory would be expected to hold in such cases where the energy of the impinging particle greatly exceeds the thermal energy of the cathode. Three cases are analyzed: first, impact by large ions which do not penetrate into the cathode; second, impact by smaller ions which may penetrate only a few layers into the cathode; and third, impact of very small high speed ions which may penetrate many layers of atoms in the cathode. The experimental values of accommodation coefficients are shown to conform sufficiently closely to the predictions of this analysis to indicate that the phenomena of loss of energy and momentum are at least approximately described by the postulates of this analysis.

INTRODUCTION

IN a recent paper by one of us[1] experiments were reported which measured the momentum transferred to a molybdenum cathode by impinging helium positive ions of known speed. These experiments, although subject to some uncertainties as a result of the many complicating factors in the electric arc, gave a measure of the accommodation coefficient for the ions at the cathode. In a paper[2] presented before the National Academy of Sciences and following the arguments of Baule,[3] reasons were given for expecting that the accommodation coefficient should be less than unity only if the mass of the metal atom composing the cathode exceeds that of the ion. It seemed of interest, therefore, to repeat the experiments referred to above for two different cathode metals, one of greater and the other of less atomic weight than the ions. The present paper is a report of these experiments for argon ions at cathodes of molybdenum and of aluminum.

APPARATUS AND EXPERIMENTAL PROCEDURE

Since a detailed description of the apparatus and experimental procedure has been given in an earlier paper,[1] a brief description only will be given here. A low voltage arc between a hot cathode and an anode was maintained in argon gas at pressures ranging between 0.004 and 0.02 mm. In the ionized atmosphere thus created was suspended the auxiliary cathode C to be studied, which was the bob of a glass pendulum whose deflection gave a measure of the force acting on the cathode. The deflection was measured by observing on a scale the position of the image of a cross-hair, the light beam having been reflected from a mirror attached to the pendulum.

The experimental procedure consisted in taking first a blank run, by way of correction for possible complicating effects, as described in the previous paper.[1] Then, with constant arc current, the deflections resulting from a change in voltage

[1] Lamar, Phys. Rev. **43**, 169 (1933).
[2] Compton, Proc. Nat. Acad. Sci. **18**, 705 (1932).
[3] Baule, Ann. de Physique **44**, 145 (1914).

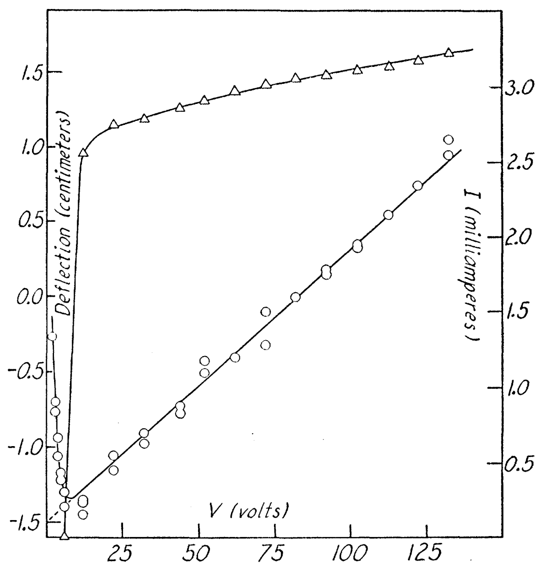

FIG. 1. Pressure per unit measured current and measured current *vs.* negative potential of the auxiliary cathode with respect to the surrounding space (argon ions on molybdenum).

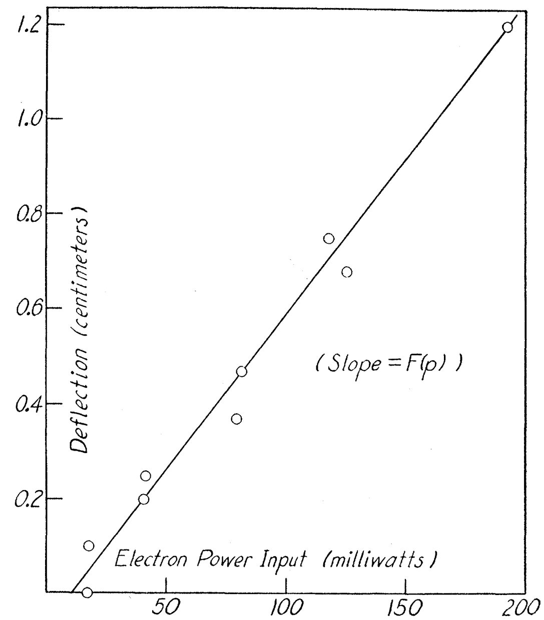

FIG. 2. Pressure resulting from electron bombardment as a function of electron power input (argon ions on molybdenum).

of the auxiliary cathode were measured. A typical set of observations is shown in Fig. 1 in which the deflection in centimeters is plotted against the negative voltage of the auxiliary cathode with respect to the surrounding space. The measured currents to the auxiliary cathode are shown on the same diagram. As the auxiliary cathode voltage is made less and less negative, a sudden change is seen to occur in both curves. This occurs when the potential of the auxiliary cathode approaches the potential of the surrounding space. The current curve indicates a large increase in electron current reaching the cathode and the deflection curve shows a correspondingly large increase in pressure on the cathode. This increase in pressure is evidently a radiometric pressure resulting from heating of the cathode by electron bombardment.

Fig. 2 shows a plot of the deflections resulting from electron bombardment *vs.* the electron power input. The slope of this curve $F(p)$ gives the radiometric pressure per unit power input when the gas pressure has the value p.

Figs. 3 and 4 show the deflections per unit measured current (positive ion current plus current of outgoing secondary electrons) *vs.* $F(p)$ for molybdenum and aluminum as determined from a series of curves of the type of Fig. 1 taken at different gas pressures.

Calculations and Discussion of Results

The pressure on the cathode resulting from ion bombardment is expressible in two terms, designated by P_1 and P_2, P_1 being an equal opposite momentum to that retained by the ions after neutralization and P_2, a radiometric pressure resulting from heating of the cathode by ion bombardment. Therefore

$$P/I = P_1/I + P_2/I$$
$$= (1-f)[C\{(1-\alpha)V\}^{\frac{1}{2}} + F(p)\alpha(V+\varphi_+)] \quad (1)$$

where f is the fraction of the current at the auxiliary cathode carried by electrons; C is a constant involving a number of known physical constants and the sensitivity of the pendulum; V is the kinetic energy, in electron-volts, of the incoming positive ions; $F(p)$ is the radiometric pressure per unit power input; α is the accommodation coefficient, and φ_+ is the work function of the cathode for positive ions. φ_+ is included in P_2 but not in P_1 since it is improbable that any energy of excitation would appear as kinetic energy of the neutralized ions.

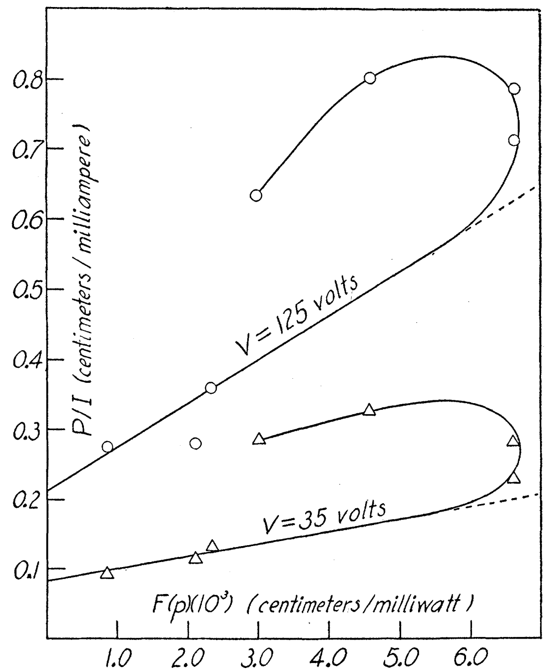

FIG. 3. Pressure per unit measured current resulting from ion bombardment *vs.* $F(p)$, the radiometric pressure per unit power input (argon ions on molybdenum).

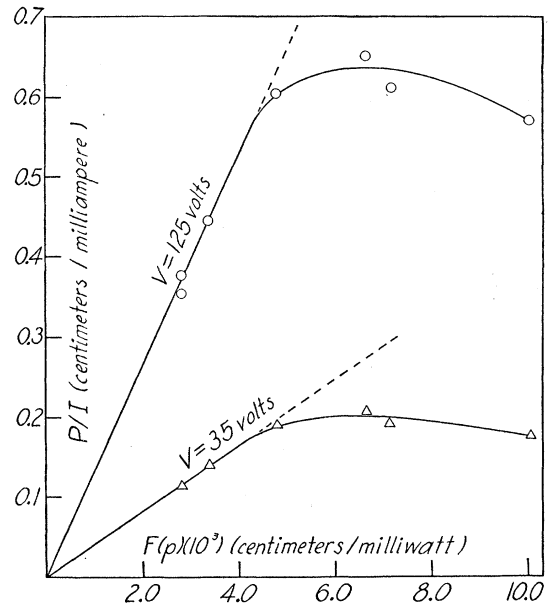

FIG. 4. Pressure per unit measured current resulting from ion bombardment *vs.* $F(p)$, the radiometric pressure per unit power input (argon ions on aluminum).

If P/I and $F(p)$ were the only variables in Eq. (1), plots of Eq. (1) under different conditions (as shown in Figs. 3 and 4) should be straight lines from the slopes and intercepts of which values of α and of f could be obtained. Since $F(p)$ has a maximum when plotted against gas pressure, there should be two sets of points on each curve, one for data obtained below and the other for data above the maximum. The rather sharp departure of these curves from linearity is believed to be due to the formation of an adsorbed layer of gas (probably argon) on the surface of the cathode. Since such a gas layer changes the nature of the surface, it may change any quantity in Eq. (1) whose value depends upon the nature of the surface. It is therefore difficult to predict the direction of deviation from linearity of the curves of Figs. 3 and 4 and it is not surprising that they should be different for the two metals investigated.

The linear portions shown in Figs. 3 and 4 were taken at low pressures where it is most justifiable to assume that the surface of the metal under investigation was free from adsorbed gas layers. Calculations of α and of f were made from the slopes and intercepts of these curves and the basis of two limiting values of φ_+, namely, 0 and $V_i-\varphi_-$ where V_i is the ionization potential of the gas and φ_- is the work function of the cathode for electrons.* The values are given in Table I. The assumption of $\varphi_+=0$ led to impossible values of f in the case of aluminum.

TABLE I.

V = negative potential of cathode with respect to space; α = accommodation coefficient; f = fraction of current carried by electrons; φ_+ = work function of cathode for positive ions; V_i = ionization potential of the gas; φ_- = work function of cathode for electrons.

	α		f	
V	$\varphi_+=0$	$\varphi_+=V_i-\varphi_-$	$\varphi_+=0$	$\varphi_+=V_i-\varphi_-$
Argon ions on molybdenum				
35	0.90	0.84	0.42	0.43
125	.83	.81	.40	.43
Argon ions on aluminum				
35	1.0	1.0	—	.031
125	1.0	1.0	—	.034

* These limiting values are set by the energy principle. If all of the energy available from the process of neutralization of a positive ion is retained by the cathode, then

Theoretical Interpretation and Conclusions

(1) Case of ions which do not penetrate the surface layer of atoms on the cathode (large and slow moving ions)

In the paper mentioned above,[2] by treating the case of single impact between elastic sphere atoms from a classical point of view, the following expression for the accommodation coefficient was given, $\alpha = 2MM_s/(M+M_s)^2$ subject to $M_s > M$, where M is the mass of the impinging ion and M_s that of the metallic atom struck. In the actual case of an ion striking a metal surface it is believed that α should be more nearly double this value as will be seen from the following argument.

In the first place, this expression with the factor 2 was derived for the impact of molecules moving under thermal motion and consequently incident at all possible angles to the surface. In dealing with ions, however, drawn in through a space charge sheath by an applied field, the ions all strike the surface perpendicularly. If they all rebound perpendicularly from head-on collisions with surface atoms, the accommodation coefficient would be

$$\alpha = 4MM_s/(M+M_s)^2, \quad M_s > M$$
$$\alpha = 1.0, \quad M_s < M.$$

Actually, however, the neutralized ion may rebound at any angle between 0 and 90° with the normal to the surface. If it rebounds at an angle near 90°, it will collide a second time with a neighboring atom of the surface layer and it leaves the surface after having made two collisions, each of them involving some loss in kinetic energy through transfer of momentum. If it strikes a surface atom more nearly head-on, it will rebound at some small angle with the normal to the surface and will strike only one atom. What we measure experimentally is, of course, a weighted mean of these possibilities.

Considering first the case of a single impact with rebound between 0 and 90° with the normal, Compton and Langmuir[4] have shown that the fraction of the kinetic energy of an impinging spherical particle which is transferred on a collision specified by the angle θ is

$$f_\theta = 4MM_s/(M+M_s)^2 \cos^2\theta,$$

where θ is the angle made by the original trajectory of the impinging particle and the radius vector from the center of the particle struck to the point of impact. The following relationship holds between θ and φ.

$$M[\sin(\varphi-\theta)\sin(\varphi+\theta)+\sin^2\theta] = M_s[\sin^2(\varphi-\theta)-\sin^2\theta]$$

where φ is the angle made by the original and final trajectories of the impinging particle.

On substituting the masses of argon and molybdenum atoms, respectively, for M and M_s, it is found that the rebound at $\varphi = 90°$ is given when $\theta = 32°\,42'$. Multiplying f_θ by the probability of a collision specified by θ, integrating between the limits imposed by the condition $\varphi \lessgtr \pi/2$, and substituting the values of M_s and M, we have,

$$\alpha = \frac{4MM_s}{(M+M_s)^2} \frac{\int_0^{32°\,42'} 2\pi \sin\theta \cos^3\theta d\theta}{\int_0^{32°\,42'} 2\pi \sin\theta \cos\theta d\theta} \tag{2}$$
$$= 0.830 \times 0.854 = 0.709.$$

We see, therefore, that the accommodation coefficient would be 0.830 if all collisions of ions were of the "head-on" type with metal atoms but would be 0.709 if all angles of rebound between 0 and 90° are considered as the result of *single* collisions only.

As has been pointed out above, however, those collisions which are relatively far from the "head-on" type involve another collision with a second surface atom. The effect of the second collisions is to increase the total energy loss and bring the accommodation coefficient nearer to

$\varphi_+ = V_i - \varphi_-$. If, however, all of this energy leaves the cathode as radiation and/or as excitation energy of the departing neutralized ion, then $\varphi_+ = 0$. There is some evidence that the true intermediate value may depend somewhat on angle of incidence. It must also depend on the extent to which this residual energy is adequate for an excited or metastable state. In all measurements which have been made of accommodation coefficient the value calculated from $\varphi_+ = V_i - \varphi_-$ gives somewhat the more consistent results.

[4] Compton and Langmuir, Rev. Mod. Phys. **2**, 210 (1930).

unity. It is easily shown, for example, that the average case of a double collision, namely, a first deflection at 90° and a second deflection back again perpendicularly to the surface, involves a total loss of energy by the impinging particle which is almost exactly the same as that which would have occurred by a single head-on collision. Thus we see that the actual accommodation coefficient is the weighted mean of one group which have collided nearly head-on and which contribute to the accommodation coefficient values between 0.830 and some lower value intermediate between 0.83 and 0.709, and a second group which have collided twice with a net contribution of about 0.830. Consequently, it is evident that the actual value of the accommodation coefficient should be much closer to 0.830 than to 0.709 and to a close approximation the value 0.830 for head-on collisions may be taken to represent the predictions of the theory.

(The further refinement of these considerations depends upon more accurate knowledge than we now have of the relation of the effective sizes of the atoms and ions and the spacing between atoms in the surface layer of the cathode.)

The experimental values of this accommodation coefficient are reported by Compton and Van Voorhis[5] as 0.75 and are found in the present investigation to be very close to 0.83. Consequently the results are in excellent agreement with the theoretical expectations.

(2) Case of slight penetration of impinging ions into cathode (small ions at moderate speeds or moderate sized ions at high speed)

In these cases the spacing between atoms of the metal may roughly be considered as greater than the diameter of the impinging ion, so that there will be a certain probability that the ion will collide in any particular layer. If α_0 is the fraction of the energy of an impinging particle which is transferred at a single collision, it is easily shown that

$$\alpha=\alpha_0 \sum_{n=1}^{\infty} (1-\alpha_0)^{n-1} P_n,$$

where P_n is the probability that an impinging particle will make n collisions before its escape from the metal.

The collision probabilities in this equation can be calculated roughly if one resorts to what amounts to a crude system of averaging. Let us assume that in any layer of the metal lattice an impinging particle either makes a head-on collision with an atom of the lattice, or passes through the layer without having suffered any collision at all. If the metal is considered as of infinite thickness, obviously each impinging particle will eventually suffer one collision and therefore $P_1=1$. After the first collision the impinging particle reverses its direction and may escape from the metal without a second collision. Let σ be the probability of collision in a particular layer. The probability that an impinging particle will collide first in the ath layer and second in the bth $(b<a)$ is obviously

$$P_{ab}=\sigma^2(1-\sigma)^{a-1}(1-\sigma)^{a-b-1};$$

$$\therefore \qquad P_2=\sigma^2 \sum_{a=2}^{\infty} \sum_{b=1}^{a-1} (1-\sigma)^{a-1}(1-\sigma)^{b-1}$$

or changing variable

$$P_2=\sigma^2 \sum_{p=1}^{\infty} \sum_{q=0}^{p-1} (1-\sigma)^{p}(1-\sigma)^{q}.$$

The summations can be carried out as a system of geometric progressions yielding

$$P_2=(1-\sigma)/(2-\sigma)$$

as the probability of two collisions within the metal.

Since after an even numbered collision the impinging particle is travelling back into the body of the metal and will thus make another collision, the probability of any odd numbered collision is equal to that of the preceding even numbered collisions.

$$P_3=P_2, \quad P_5=P_4, \quad \text{etc.}$$

In a similar way to that described above, the probability of four collisions can be written down as

$$P_4=\sigma^4 \sum_{a=2}^{\infty} \sum_{b=1}^{a-1} \sum_{c=b+1}^{\infty} \sum_{d=1}^{c-1} (1-\sigma)^{a-1} \times(1-\sigma)^{a-b-1}(1-\sigma)^{c-b-1}(1-\sigma)^{c-d-1}$$

[5] C. C. Van Voorhis and K. T. Compton, Phys. Rev. **35**, 1438 (1930); Phys. Rev. **37**, 1596 (1931).

or, changing variables

$$P_4=\sigma^4\sum_{p=1}^{\infty}\sum_{q=0}^{p-1}\sum_{r=0}^{\infty}\sum_{s=0}^{r+p-q-1} \times(1-\sigma)^p(1-\sigma)^q(1-\sigma)^r(1-\sigma)^s.$$

This expression can be reduced since each step in the reduction involves a known summation. The final result is

$$P_4=(1-\sigma)/(2-\sigma)\{1-(1-\sigma)^3/(2-\sigma)^2\}.$$

The calculation of these collision probabilities becomes increasingly laborious for each successive collision and in the present paper the calculations have not been carried beyond five collisions. Substitution of these in the expression for α yields

$$\alpha=\alpha_0[1+(1-\alpha_0)(2-\alpha_0)\{(1-\sigma)/(2-\sigma)\} \times\{\alpha_0(2-\alpha_0)-(1-\alpha_0)^2(1-\sigma)^3/(2-\sigma)^2\}]+\cdots.$$

The experimental value of α given by Compton and Van Voorhis[5] for neon ions on molybdenum is 0.65. This is greater than the value of α (slightly less than 0.57) to be expected from a single collision by Eq. (2), which fact indicates some possible penetration of the ions beyond the first layer of atoms of the metal, i.e., multiple collisions. The above expression for α gives good agreement with the experimental value if we assume that $\sigma=0.64$. This is equivalent to saying that the process is equivalent to head-on collisions by 64 percent of the incoming ions in the first layer of the metal; the remaining 36 percent go on to the second layer where 64 percent of them collide, and so on.

Attempts to apply the above theory to the case of helium ions on molybdenum have been unsuccessful probably for the reason that there may be so much penetration of the ions into the metal that five collisions are by no means sufficient to account for the energy transferred. That this penetration does occur was proven by experiments of Langmuir and his colleagues, who showed that metal cathodes will absorb relatively large quantities of helium incident in the form of bombarding ions and that this helium may subsequently be driven out by heating the cathode. The amounts of helium thus absorbed may be equivalent to many layers deep of atoms over the surface, which indicates that the ions may penetrate considerable distances. Under these circumstances the following argument appears to be a more satisfactory approximation than the one preceding.

(3) Case of ions which penetrate deeply into the cathode (helium or hydrogen ions at high speed)

If, as a first approximation, the ions are scattered like elastic spheres, there should be a high degree of randomness of motion after the first collision, approaching a completely random distribution if the mass of the ion is very small in comparison with that of the metal atoms. We will therefore assume a completely random direction of motion in the metal after the first collision. The probability that an ion will travel into the metal a distance x and collide in dx at x is

$$P_1=\mu_1 e^{-\mu_1 x}dx.$$

Then, after the first collision, the ions will be divided into two groups; those which are travelling toward the surface of the metal and those which are travelling toward the interior. Although an ion may on collision change from one of the above groups to the other, there should be an equal probability of a reverse change for one of the other group, so that, on the average, the grouping will remain unaltered. Those ions which travel into the metal will lose all of their energy before their ultimate escape. Those ions which travel out from the metal after the first collision will travel a distance greater than x in going the perpendicular distance x. The probability that an ion, which has made its first collision in dx at x, will make n collisions before escaping from the metal is

$$P_2=[(\mu_2 x)^n/n!]e^{-\mu_2 x},$$

where μ_2 is the reciprocal of the normal component of mean free path as the ion moves toward the surface.

If an ion retains a fraction f of its energy at a collision, then the total fraction of the initial energy of all the incoming ions which escapes from the metal with those ions which have made their first collision in the layer dx at x is

$$dF=c_1 f\mu_1 e^{-\mu_1 x}\sum_{n=1}^{\infty} f^n\frac{(\mu_2 x)^n}{n!}e^{-\mu_2 x}dx,$$

whence the fraction of all the energy of the incoming ions which escapes from the metal, is given by

$$F=c_1f\mu_1\sum_{n=1}^{\infty}\frac{f^n}{n\,!}\int_0^{\infty}(\mu_2x)^n e^{-(\mu_1+\mu_2)x}dx$$

$$=\frac{c_1f^2\mu_1\mu_2}{(\mu_1+\mu_2)(\mu_1+\mu_2-f\mu_2)}.$$

$$\therefore \quad \alpha=1-F=1-\frac{c_1f^2\mu_1\mu_2}{(\mu_1+\mu_2)(\mu_1+\mu_2-f\mu_2)}.$$

The constant c is the grouping constant, i.e., the fraction of the ions which travel toward the surface of the metal after the first collision. If the scattering were completely random, c_1 would be $\frac{1}{2}$. (This would be accurate for the particles of infinitesimal weight colliding with elastic spheres but would be progressively less accurate as the mass of the ion approaches that of the metal atoms. It is, however, a fair assumption to make for the case of small penetrating particles like hydrogen or helium.)

With the same degree of approximation as leads to $c_1=\frac{1}{2}$, we may assume that the average particle moving toward the surface moves twice as far as if it escaped normally, so that we may take the ratio μ_2/μ_1 to be approximately 2. With these rough approximations and taking

$$f=1-2MM_s/(M+M_s)^2$$

we have for helium on molybdenum

$$\alpha=1-0.852\times 2/[2\times 3(3-1.845)]=0.754.$$

This value should be an upper limit to the accommodation coefficient and would be appropriate for very high speed ions, since the collision radius becomes small at very high velocities.

Actually we have a variety of values reported for helium. For helium atoms thermally incident on a clean tungsten surface, Roberts[6] gives a value 0.06, while Michaels[7] reports 0.17. Getting, in some unpublished work very recently performed in this laboratory, has checked closely the value given by Roberts. These values are in excellent agreement with the value 0.067 which would be calculated by the methods of Eq. 2 for the impact of nonpenetrating particles.

On the other hand, the accommodation coefficient of helium ions incident on molybdenum has been found to range between 0.35 and 0.55, with indication that the larger values are characteristic of ions of higher velocities (this is in accordance with the values of Van Voorhis and Compton[5] and also the values of Lamar,[1] where an indication of a reversed variation at higher velocities is probably attributable to the effect of collisions within the space charge sheath at the larger voltages).

We thus find in the case of helium, values of accommodation coefficient which are of the order of magnitude of those to be expected for nonpenetrating or penetrating conditions under just those circumstances in which it is known experimentally that the helium does not or does penetrate into the metal.

Just as in specific heats at high temperatures the classical picture of collisions appears to be adequate to explain momentum and energy transfers when high speed particles like ions strike a surface. For large ions there appears to be no appreciable penetration beyond the first layer of surface atoms but there is some evidence of scattering at various angles and double collisions at the rebound. For small ions like neon, and much more with helium, there is evidence of penetration into the cathode in the process of neutralization and rebound.

[6] Roberts, Proc. Roy. Soc. **A135**, 192 (1932).

[7] Michaels, Phys. Rev. **40**, 472 (1932).