One expands to first order (while changing to dimensionless variables) and obtains

$$\varphi_1=\varphi_0\{1+(\delta_n-\tfrac{3}{2}\delta_T)+2\delta_v\zeta+\delta_T C^2\}. \tag{15.2}$$

If we compare this result with (5.6), we see that $\delta_n-\frac{3}{2}\delta_T=\beta$, $2\delta_v=\mu$, and $\delta_T=\epsilon$.

The interface conditions (14.13)–(14.15) express the number and momentum flux relations which hold at the barrier. Let us now assume that there is no decaying part ψ to Ψ. Then the interface conditions reduce to

$$\mu_V=\exp(-\zeta_0^2)\mu_L, \tag{15.3}$$

$$\tfrac{1}{2}\beta_V+(5/4)\epsilon_V=\tfrac{1}{2}\beta_L+\epsilon_L[\tfrac{3}{4}+\tfrac{1}{2}\zeta_0^2+\tfrac{1}{2}\exp(\zeta_0^2)], \tag{15.4}$$

$$\begin{aligned}2I_\beta\beta_V+2I_\epsilon\epsilon_V=\exp(\zeta_0^2)\{(\tfrac{1}{2}-2I_\beta^<)\beta_L&\\-2I_\mu^<\mu_L+(5/4-2I_\epsilon^<)\epsilon_L\},&\end{aligned} \tag{15.5}$$

where

$$I_\beta\equiv(2\pi^{\frac{1}{2}})^{-1}\{\zeta_0+\exp(\zeta_0^2)G(\zeta_0)\}, \tag{15.6}$$

$$I_\mu\equiv\pi^{-\frac{1}{2}}\exp(\zeta_0^2)H(\zeta_0), \tag{15.7}$$

$$I_\epsilon\equiv(2\pi^{\frac{1}{2}})^{-1}\{(5/2-\zeta_0^2)[\zeta_0+\exp(\zeta_0^2)G(\zeta_0)+\zeta_0^3\}, \tag{15.8}$$

and

$$G(\zeta_0)\equiv\int_{\zeta_0}^\infty \exp(-u^2)du;$$

$$H(\zeta_0)\equiv\int_{\zeta_0}^\infty \exp(-u^2)\{u^2-\zeta_0^2\}^{\frac{1}{2}}u^2du.$$

Also

$$I_\beta^<\equiv(2\pi^{\frac{1}{2}})^{-1}\{\tfrac{1}{2}\pi^{\frac{1}{2}}-\zeta_0\exp(-\zeta_0^2)-G(\zeta_0)\}, \tag{15.9}$$

$$I_\mu^<\equiv(2\pi^{\frac{1}{2}})^{-1}\{1-\exp(-\zeta_0^2)\cdot(1+\zeta_0^2)\}, \tag{15.10}$$

$$\begin{aligned}I_\epsilon^<\equiv(2\pi^{\frac{1}{2}})^{-1}\{\tfrac{1}{2}\pi^{\frac{1}{2}}-\zeta_0&\\\times\exp(-\zeta_0^2)\cdot(1+\zeta_0^2)-G(\zeta_0).&\end{aligned} \tag{15.11}$$

These are the relations that appear in the elementary evaporation theory[11] for slow evaporation. Therefore, the present treatment is a correction to the elementary theory for this case.

16. ACKNOWLEDGMENT

My thanks are due Professor L. Onsager for suggesting this problem and for helpful discussions.

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[11] G. Dieterici, Ann. Physik N. F. **66**, 826 (1898).

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Electron Ejection by Slow Positive Ions Incident on Flashed and Gas-Covered Metallic Surfaces

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A direct measurement of the ejected electron yield (γ_i) for A^+ incident on flashed and H_2-, N_2- and O_2-treated Ta and Pt and for the singly-charged hydrogen, nitrogen, and oxygen ions incident on Ta and Pt after treatment with the respective parent gas has been made for the kinetic energy range of 2 to 150 ev. The gas treatment for Pt consisted of an exposure to the molecular gas at a pressure of a few mm of Hg, while the treatment for Ta consisted of an exposure plus a glow discharge in which the Ta surface served as the cathode. In general, gas treatment of Ta and Pt was found to produce large decreases in γ_i for A^+ ions, with the effect increasing with decreasing ion energy. For both Ta and Pt the O_2 treatment was found to be the most effective in reducing γ_i while the H_2 treatment was found to be the least effective. γ_i for nitrogen ions on N_2-treated Ta and Pt showed a unique behavior at low ion energy in that it was found to increase with decreasing ion energy. This behavior was not observed for the other ions in this study.

I. INTRODUCTION

THE electrical breakdown of gases is dependent on a primary and a secondary mechanism. Of the active secondary mechanisms, one is photoelectric ionization in the gas near the anode and three more consist of electron liberation from the cathode by photons, metastable atoms, and positive-ion impact. The liberation by positive-ion impact is not only the first of these mechanisms invoked, but it is also exceedingly important for many discharges. Various means have been devised for evaluating γ_i, the coefficient of secondary electron liberation from the cathode, extending from discharge studies to measurements by static or dynamic means in the presence of a gas. Such studies suffer from inadequate control of variables, inability to differentiate between different cathode effects in static studies, and electron loss by back diffusion. The significant first direct studies of the number of electrons liberated per positive ion impact in vacuums with clean electrodes were those of Jackson[1] and more *in extenso* those of Oliphant, and Oliphant

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* This work was initially supported under a contract with the U. S. Office of Naval Research. It was carried to its successful conclusion under a grant from the National Science Foundation.

[1] W. J. Jackson, Phys. Rev. **28**, 524 (1926).

and Moon.[2] Further studies of this nature have over the years been carried on by Paetow and Walcher,[3] Penning,[4] Rostagni, Helea, and Houtermans, and Hagstrum.[5] The theory of the process has been treated by Kapitza,[6] Oliphant and Moon,[7] Massey,[8] Shekhter,[9] Cobas and Lamb,[10] Hagstrum[11] and Varnerin.[12]

All of these studies dealt with clean metallic surfaces largely with ions above some 50 volts kinetic energy. Although it was recognized that liberation could occur at low kinetic energies of impact if the ionization potential lay above the work function of the surface, (potential liberation), only limited measurements for ions of low kinetic energy had been made when this study began. However, there are many discharges in which secondary cathode emission occurs where ions have energies of the order of 10 volts and perhaps less. Furthermore, little attention was paid in these studies to gas-coated surfaces.

In the electrical breakdown of gases, various gases are obviously present and these tend to create surface films on the cathodes while positive-ion bombardment tends to remove these films. It thus becomes of importance to study the secondary emission from clean and gassy surfaces on cathodes in order to determine the sort of changes to be expected in secondary emission under discharge conditions. So far only Paetow and Walcher[3] using 500-volt Cs^+ ions on W and W coated with Cs, K, O_2, and H_2 and Hagstrum[5] using 200-volt He^+ and Ne^+ ions on H_2- and O_2-coated W as well as He^+ on Mo covered by the condensation of background gases under high vacuum conditions, have attempted such studies. The work of Hagstrum[5,11] was begun and carried out nearly contemporaneously with this investigation.[13] Accordingly this study was undertaken to investigate the secondary electron emission by various ions on clean and contaminated surfaces, using common gases and various ions with energies ranging from about two volts up to two hundred volts. Adopting the very efficient Finkelstein[14] type of ion source producing ion beams of low-energy spread, which permits operation at low gas pressures without differential pumping, direct measurements of γ_i, the positive ion impact coefficient for A^+ ions incident on flashed Ta and Pt as well as on these metals after treatment with H_2, N_2, and O_2 gases, were made. In addition, measurements were made on these metals after exposure to the appropriate gas with singly-charged hydrogen, nitrogen, and oxygen ions.

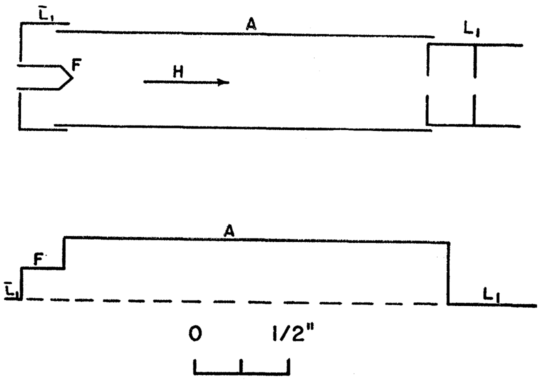

FIG. 1. The Finkelstein ion source above, with relative potentials applied to corresponding electrodes below.

II. EXPERIMENTAL PROCEDURES

A. The Positive Ion Source

The source was of the Finkelstein[14] type shown in Fig. 1 with a diagram of the relative electrode potentials drawn below. In principle the electrons from the hot W filament F are accelerated along the axis of the tubular electrode A by an appropriate potential V_{FA} between A and F. An axial field H of a few hundred gauss causes the electron paths to spiral while the repeller plate L_1 with an aperture and a retarding field relative to A repels electrons and extracts positive ions. At 10^{-5} mm Hg pressure of argon gas with a few μa of electron

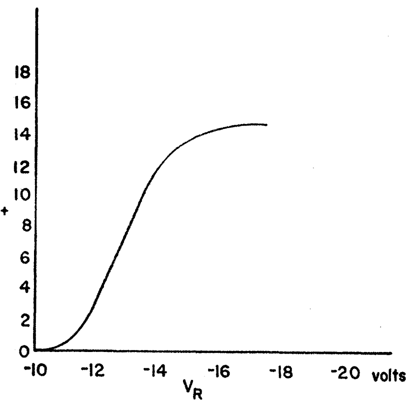

FIG. 2. Retarding potential curve showing two-volt energy spread of ion beam.

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[2] M. L. E. Oliphant, Proc. Cambridge Phil. Soc. **24**, 451 (1928); M. L. E. Oliphant and P. B. Moon, Proc. Roy. Soc. (London) **A127**, 373 (1930).

[3] H. Paetow and W. Walcher, Z. Physik. **110**, 69 (1938); W. Ploch and W. Walcher, Z. Physik. **130**, 174 (1951).

[4] F. M. Penning, Proc. Roy. Acad. Sci. (Amsterdam) **31**, 14 (1928); **33**, 841 (1930); Physica **8**, 13 (1928); A. Rostagni, Ricerca sci. **9**, 633 (1938); M. Helea and C. Houtermans, Phys. Rev. **58**, 608 (1940); M. Helea and E. L. Chaffee, Phys. Rev. **49** 925 (1936); I. Okano, J. Phys. Soc. Japan **8**, 362 (1953).

[5] H. D. Hagstrum, Phys. Rev. **89**, 338 (1953).

[6] P. L. Kapitza, Phil. Mag. **45**, 989 (1923).

[7] M. L. E. Oliphant and P. B. Moon, Proc. Roy. Soc. (London) **A127**, 388 (1930).

[8] H. S. W. Massey, Proc. Cambridge Phil. Soc. **26**, 386 (1930); **27**, 460 (1931).

[9] S. S. Shekhter, J. Exptl. Theoret. Phys. (U.S.S.R.) **7**, 750 (1937).

[10] A. Cobas and W. E. Lamb, Phys. Rev. **65**, 327 (1944).

[11] H. D. Hagstrum, Phys. Rev. **89**, 244 (1953); **91**, 541 (1953).

[12] L. J. Varnerin, Jr., Phys. Rev. **91**, 859 (1953).

[13] Quite contemporaneous with this study was one of Okano (see reference 4) in Japan using Mo with common gases at high energies. The results roughly parallel those here although the outgassing and vacuum techniques were not comparable with those of either Hagstrum or the writer.

[14] A. T. Finkelstein, Rev. Sci. Instr. **11**, 97 (1940).

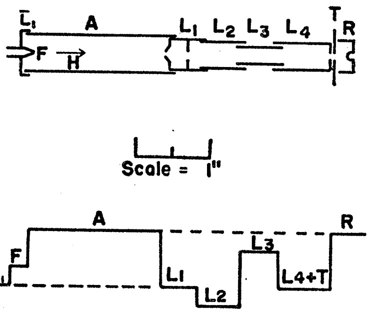

FIG. 3. Tube No. 1 above, with relative applied potentials below.

current from F, the ion beam has a strength of approximately 10^{-8} amp.

The energy spread of the ion beam from this source was about 2 ev as seen in the typical retarding potential curve shown in Fig. 2. From the retarding potential measurements, the potential at which the ions were produced in the source and therefore the energy of the electrons producing them could be ascertained. Thus it appeared that the potential at which the ions were produced was about 10 volts below the potential of electrode A. Experiments revealed that if the electron energy was below 28 ev the ions produced were A^+. Above this, A^{++} ions created by a two-stage process were also present. Thus all measurements were made below 28-ev electron energy. While through the Molnar-Hornbeck[15] process A_2^+ ions might have formed, with pressures of 2×10^{-5} mm these constituted less than 0.5 percent of the total beam. In the measurements of γ_i for ions of gases H_2, N_2, and O_2, the same energy of 28 ev was used. Therefore, while both atomic and molecular ions were present in unknown proportions, only singly-charged ions were produced.

B. The Experimental Tubes

Two tubes were used and these are shown respectively in Figs. 3 and 4. In Fig. 3 the relative potentials on the electrodes are shown below the electrode diagram. All electrodes except the target T were made of Ta sheet (0.015 in. thick) and were cylindrically symmetric. In tube 1 the target T was a rectangular sheet $\frac{1}{2}$ in.$\times$1 in. and 0.00025 in. thick with a circular hole which could be heated by conduction currents. Here R was a repeller electrode at such potential that no positive ions could reach it. The secondary electrons from impact of positive ions on T were drawn to R. L_2 at 10 volts negative to L_1 prevented secondary electrons at L_1 from reaching R. L_3 cut off the lower-energy tail of the positive ion beam. L_4 at the same potential as T prevented positive ions from striking the back side of T. The diameters of holes in L_2 and L_3 were larger than L_4.

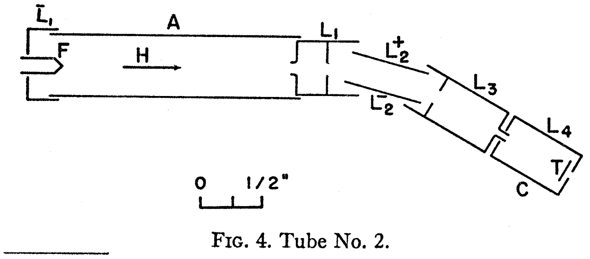

FIG. 4. Tube No. 2.

The retarding potential measurements on the positive ion beam were made by using R as the retarding electrode for ions that pass through L_4 and T. Figure 2 represents the ion current to R as a function of the potential of R with respect to A. Then the potential at which cutoff occurs is the potential with respect to A at which the ions are formed in the source. Both positive ion current to T and electron current to R were measured by separate electrometer tube circuits and potential sources were batteries and potentiometers. Tests ascertained that less than 1 percent of the ejected electrons were returned to the surface by the magnetic field for angles between the normal to the surface and magnetic field from 0 to 45°.

Tube 1 had two defects, these being that the angle of incidence of positive ions on the target was not defined and that secondary electrons produced at L_4 were recorded at R as apparent secondaries from T. Since emission could depend on angles of incidence and as this would generally vary with ion energy, the data on emission as a function of energy were in doubt. That trouble might come from L_4 as secondaries was indicated when a small retarding field for electrons between L_4 and T decreased γ_i by 30 percent. After recourse to tube 2 which avoids these difficulties checked the data on Ta to within 5 percent it was realized that the decrease caused by retarding field on L_4 probably came from positive ions striking the back of the target so that the results were not in doubt.

The source in tube 2 was the same except that the magnetic field of $H\sim200$ gauss was longer in order to envelope the whole electrode assembly. L_2^+ and L_2^- were half-cylinders which acted as deflecting plates. L_3 was a cylinder with two collimating apertures, while L_4 and C were two half-cylinders capped at the ends and separated by 1 mm. The caps toward L_3 formed a circular aperture collinear with those of L_3. Target T was a sheet of $\frac{3}{16}$ in.$\times\frac{3}{8}$ in.$\times$0.00025 in. for Ta and a similar sheet of 0.0004 in. for Pt, placed perpendicular to the axis of L_4 and C which could be heated by conduction currents.

Here the incidence of the beam on the target is normal. If C is positive to T all electrons from T follow the magnetic field and go to C. Electrons from the last aperture in L_3 will be collected by L_4. Excited and metastable atoms from the source are prevented from reaching T. This new arrangement also had its deficiencies as regards the proper potential distributions for L_3, L_4, and C in order to obtain correct data on γ_i for low ion energies. Thus if T was 15 volts or more

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[15] J. A. Hornbeck and J. P. Molnar, Phys. Rev. 84, 621 (1951).

negative to the formation potential of the ions in the source and with C set so that ions could not reach it, ions reached T if L_4 was a few volts negative to C. For lower energies the potential of C was lowered so that ions could reach T. However, this meant that ions could now reach C, but by increasing the potential difference between C and L_4 the ions were sufficiently deflected so that measurements extended down to 5 volts.

With the potential of L_4 and C equal and sufficiently negative to T so that ejected electrons from T could not reach them, a positive current was measured at C of 1 percent of the target ion current. This gave an upper limit to the reflection coefficient of positive ions from T. This low value is in qualitative agreement with observations by Hagstrum.[1]

That all electrons ejected from T were collected by C is indicated by results with flashed Ta using He^+ ions which agreed with measurements of Hagstrum[11] under similar conditions to within 7 percent.

C. Vacuum System and Gases

A schematic diagram of the vacuum system is shown in Fig. 5. The vacuum techniques and pressure measurements closely followed those developed by Alpert,[16] the metal valves and ion gauges being on an all borosilicate glass system which could be baked out at 400°C. One Alpert valve served as cutoff, the other as a slow leak. The electrodes of the gauge were outgassed by electron bombardment while those of the measuring tube were outgassed by induction heating. The target could be flashed by conduction current. Absorption and source gases were contained in glass bottles of 2-cc capacity, opened by magnetic-slug-activated breakoffs. Figure 6 shows a photograph of the whole assembly, which is remarkably compact.

The argon came from Linde's one-liter flasks of spectroscopically pure argon. The N_2 and H_2 were prepared by circulating Linde tank gases over hot Cu and through liquid N_2 traps for 24 hours. The O_2 was simply tank O_2 passed through and distilled from a liquid N_2 trap.

D. Procedures

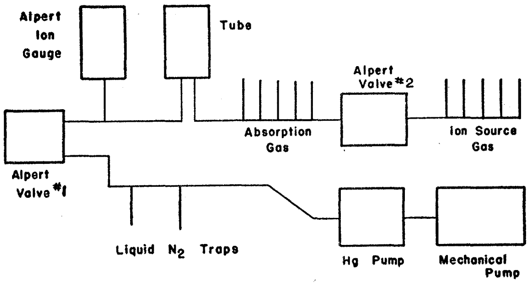

FIG. 5. The vacuum system.

The system was baked at 400°C for periods of 12 to 24 hours. The oven was shut off and the electrodes of the tube were induction heated to 700°–900°C. Pressures at this time with all electrodes cold except the source filament usually ran to $2\text{–}5\times10^{-9}$ mm Hg, (equivalent-N_2 pressure.) Repeated flashing of the target from 30 seconds to several minutes was continued until the maximum pressure after a flash was not over $1\text{–}2\times10^{-8}$ mm Hg. For Pt the flash temperature was 1400°C, while for Ta it was 1400–2000°C. Within a few seconds after flash pressures returned to 10^{-9} mm. When ready the Alpert valve 2 was closed and the source bottle opened. The valve 2 was then opened until the pressure in the tube was $2\text{–}3\times10^{-5}$ mm Hg. Then measurements of γ_i for A^+ began. After study of flashed clean surface, both valves were closed and an absorption bottle was opened, the pressure rising to a few mm of Hg. The Pt was merely exposed to H_2, N_2, or O_2 for 5 minutes except in one case of a 5-minute exposure with 1 minute of glow discharge between target and collector using tube No. 2. In tube No. 1 with Ta target exposure plus glow discharge was routine.

After gas treatment, valve 1 was opened and the absorption gas pumped out to low pressure, or to operating pressure when absorption gas ions were to be used. If A^+ ions were used, the tube after pump-out of absorption gas was filled with A up to operating pressure by opening valve 2. Between each gas treat-

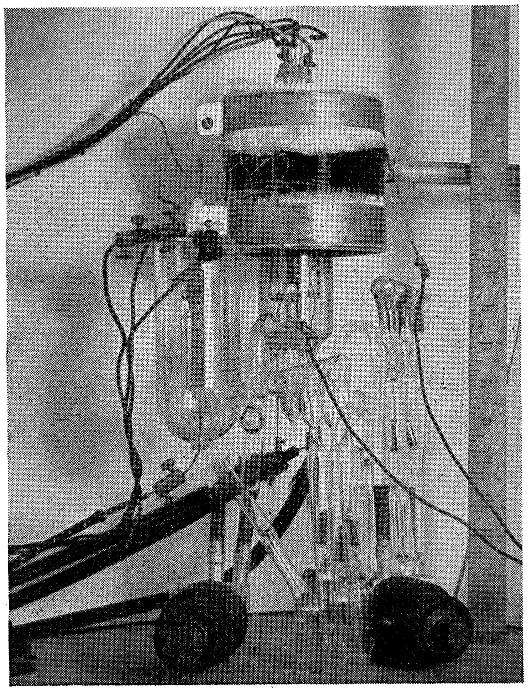

FIG. 6. The whole assembly showing vacuum techniques, and simplicity possible by Finkelstein-type source.

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[16] D. Alpert, Rev. Sci. Instr. 22, 536 (1951); J. Appl. Phys. 24, 860 (1953); R. J. Bayard and D. Alpert, Rev. Sci. Instr. 21, 571 (1950).

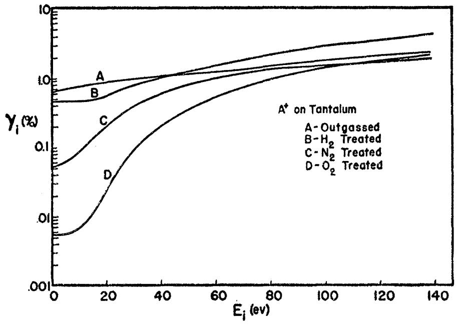

FIG. 7. Ejected electron yield (γ_i) for A^+ ions on outgassed and H_2-, N_2-, and O_2-treated Ta. Note rise to high values irrespective of gas above 100 ev.

ment the entire baking and outgassing procedure was repeated. In operating tube 1 the background pressure during taking of data was in the high 10^{-8} mm range, while that in tube 2 was always between 2 and 5×10^{-9} mm. Measurements in tube 2 could begin 25 seconds after flashing, while in tube 1 they began only after 10 minutes.

III. RESULTS AND DISCUSSION

A^+ on Tantalum

The results obtained with tube No. 1 for A^+ incident on flashed and gas-treated Ta is shown in Fig. 7. Curve *A* is representative of the data obtained after heating and flashing the Ta target to 1400°C. Data taken on different days, for the same target condition, never deviated from that represented by curve *A* by more than ±5 percent. The drift in the value of γ_i after flash was found to be slow and small. With the target cold for an hour after the flash, the maximum change in γ_i was always less than 20 percent and for a 24-hour cold period the change was found to be only 30 percent. At the time of these measurements it was thought that if the surface gas had been removed as a result of the flash, either the film had reformed before measurement was possible and the slow drift was a result of the low sticking coefficient for gas atoms on a covered surface, or that the partial pressure of adsorbable gas in the background was so low that slow redeposition took place even though the surface was clean. That the first alternative was not unlikely for a flash measurement time of ten minutes and with a background pressure in the high 10^{-8} mm Hg range, can be seen, for if one assumes unity sticking coefficient for the condensing background gas atoms, the monolayer formation time is of the order of one minute.[17,18] However, there was the possibility that the flashing did not remove the gas film and the slow drift in γ_i resulted from the low sticking coefficient of a covered surface. When a Ta target was installed in tube No. 2, not only was the slow drift in γ_i after the flash reproduced but the values obtained for γ_i were within 5 percent of those obtained with tube No. 1. The conditions with tube No. 2 were such that it seemed unlikely that the gas film had *re-formed* before measurement. Therefore, either the gas film was not removed as a result of the flash, or the slow drift was to a low sticking coefficient of the additional atoms, or the film was removed and the slow drift was due to a low partial pressure of adsorbable background gas. The first possibility coincides with Hagstrum's[11] conclusions from recent work on electron ejection by He^+ ions on Ta. From his observations he was forced to conclude that a basic gas film on Ta is not removed by flashing to 1475°C but at the time of the flash it enters into the metal and then returns to the surface as the metal cools. Therefore it seems likely that curve *A* in Fig. 7 is for gas covered Ta and the small drift observed in γ_i after flash was due to the addition to the already covered surface of a few less tightly held atoms. As an added check on the state of the Ta surface used in these studies as compared with that in Hagstrum's studies, a measurement was made of γ_i for He^+ on Ta with tube No. 2. Hagstrum[11] had found γ_i to be essentially constant over the ion energy range of 10–150 ev and equal to 14 percent. With tube No. 2 a constant value of 13 percent was obtained for this same ion energy range.

The only work with which the results for A^+ on Ta may be compared is the pulsed Towsend discharge study by Molnar.[18] In this work for argon and a Ta cathode the value of γ_i at various E/p and p was found to range from 0.5 to 2.6 percent. These results are to be compared with the value of 0.7 percent, obtained in the present study for ions with an energy of a few ev.[19]

The results obtained after gas treatment are shown by curves *B*, *C*, and *D* in Fig. 7. When measurements were started after each gas treatment, γ_i was found, at least for the lower ion energies, to drift slowly upward. This was undoubtedly due in part to the sputtering action of incident argon ions. It is to be noted that after the N_2 and O_2 treatment, γ_i for low ion energy was found to be smaller than that of the flashed surfaces by a factor of approximately 10 to 100, respectively, while at higher energies γ_i for treated surfaces tended to coincide with that obtained for the flashed surface. After the H_2 treatment, γ_i was found to be smaller

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[17] This assumes that the gas adsorbed by the target is the background gas and not impurities in the argon or the argon itself. Mass spectrometric analysis of Linde's "spectroscopically pure" argon by Molnar (see reference 18) have shown the impurities to be less than 0.005 percent. This figure would mean that the partial pressure of impurities introduced with the argon would be in the 10^{-9} mm Hg range. While there is not evidence that the thermal argon atoms are adsorbed at room temperature it is known that argon ions of a few ev energy are. However, the effect due to adsorption of argon as ions can be ruled out at least for tube 2 because of the short flash-measurement time (25 seconds), and the low positive-ion beam current densities ($\sim10^{-9}$ amp/cm^2 at the target).

[18] J. P. Molnar, Phys. Rev. 83, 940 (1951).

[19] Molnar's values depend critically on the values of the first Townsend coefficient which are difficult to measure, and thus may not be as reliable as direct values.

at low energy, while being found to be larger at the higher energies. Apparently in the case of the N_2 and O_2 treatment the ions of high energy can penetrate the additional film put on by the gas treatment, and can interact with the surface underneath, while for ions of lower energy the interaction tends to take place at this second film.

A^+ on Platinum

The results for A^+ incident on platinum are shown in Fig. 8. Each point of the top curve represents a measurement made 25 seconds after the target was flashed at 1400°C. With Pt a large drift in γ_i was observed to occur after the flash and a typical plot of γ_i as a function of time after flash is given in Fig. 9. Also the curve labeled "15 minutes after flash" in in Fig. 8 shows the change that has taken place in γ_i for a 15-minute flash measurement time. For the target cold for 24 hours γ_i was found to be reduced to $\frac{1}{3}$ of that obtained just after the flash. While it is not maintained that flashing Pt at 1400°C necessarily produced an atomically clean surface, the fact that a large and fast change in γ_i does occur after flash seems to indicate that at least a major part of the surface gas film was removed, the drift indicating the reformation of such. However, even if only a portion of the surface gas was removed by the flash it is still not strange that the drift is fast as contrasted with that found for Ta, since Pt is known to be an active surface catalyst for many gaseous reactions and this activity is directly connected with adsorption.

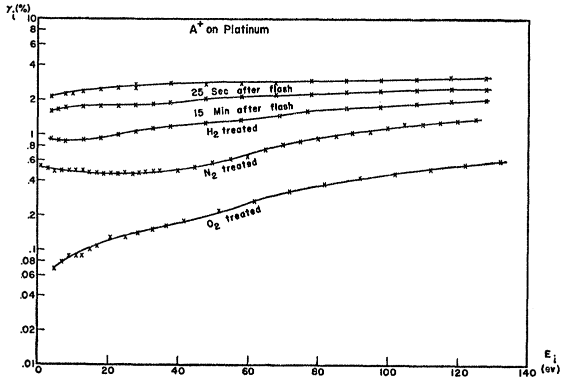

FIG. 8. Ejected electron yield (γ_i) for A^+ ions on outgassed and H_2-, N_2-, and O_2-treated Pt. Note the difference of Pt relative to Ta in that values of γ_i do not merge above 100 ev. Note also decrease in γ_i with time after flash.

The other three curves of Fig. 8 show the effect of gas treatment on γ_i for Pt. As was stated before, the treatment in the case of Pt consisted of a five-minute exposure without glow discharge. This time, along with the adsorption gas pump-out time of 10 minutes, meant the time from flash, through the gas treatment, to the measurement on the covered surface was about 15 minutes. From Fig. 8 it can be seen that in all cases the effect of gas treatment was greater than the effect due to background gas for corresponding cold target periods. Therefore the condensation of background gas did not at all mask the effect due to the intentionally introduced adsorption gases. It was observed for gas-treated Pt, as it was for gas-treated Ta, that after the start of the measurements γ_i showed a slow upward drift in the time indicating that some of the adsorbed gas was leaving the surface, due at least in part to ion bombardment. In the one exposure plus discharge treatment in N_2 carried out for Pt, the data was found to lie below that obtained after just an exposure by only about 10 percent. Also, as was the case for gas-treated Ta, the order of increasing effectiveness for the reduction of γ_i was H_2, N_2, and O_2. It is to be noted that the shape of the curves for gas-treated Pt are quite different from those of gas-treated Ta. In the case of Pt the decrease which resulted from gas treatment separated the curves from each other and from that for flashed Pt over the entire ion energy range. This is to be contrasted with the results for Ta where the curves are separated at low ion energy while at higher energy the N_2 and O_2 curves tend to coincide with the flash curve and the H_2 curve rises above.

As a tentative explanation for the difference in results for gas treated Pt and Ta, it is suggested that while with Ta the ions are easily able to penetrate the small additional gas film resulting from treatment, for Pt the treatment results in a complete film over the surface which cannot as easily be penetrated by the ions.

N_2^+ and N^+ on N_2-Treated Ta and Pt

Figures 10 and 11 show the results obtained for a mixture of N_2^+ and N^+ ions incident on N_2-treated Ta and Pt, respectively. The interesting point to be noticed in both of these figures is the increase in γ_i with decreasing ion energy at low ion energies. It would be interesting, of course, to know if this effect is characteristic of both N_2^+ and N^+ or just characteristic of one of these ions. However, in the present studies this

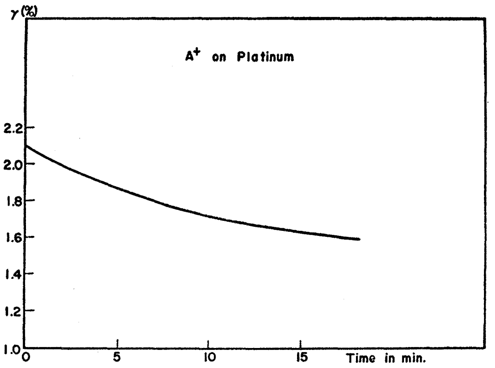

FIG. 9. Ejected electron yield (γ_i) for A^+ ions on outgassed Pt as a function of time. The decrease is due to monolayer formation caused by either residual background tube gases or impurity in the A gas.

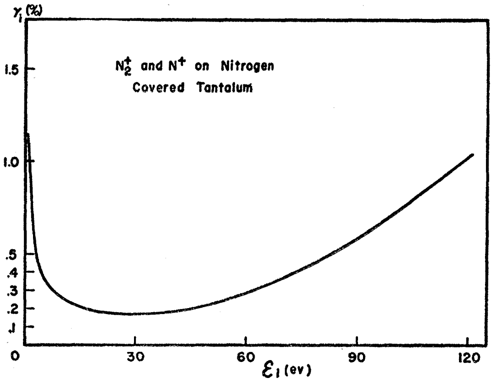

FIG. 10. Ejected electron yield (γ_i) for N_2^+ and N^+ ions on N_2-covered Ta. Note the increase in γ_i at low energies. This may come from emission caused by recombination of N at the surface.

information was impossible to obtain. Also, it is to be noted that the curves for nitrogen ions on Ta and Pt for ion energy greater than approximately 30 ev lie somewhat near the curve for A^+ on the N_2-treated Ta and Pt surfaces, respectively. This is not at all unexpected since the energy available after neutralization of the singly charged nitrogen ions is very close to that for A^+. Therefore, it would be expected that γ_i for nitrogen ions on flashed Ta without a nitrogen surface film would not differ appreciably from the data obtained for A^+ on flashed Ta.

While there is no study that can be directly compared with these results, still it is interesting to note that Huber,[20] using the pulsed Townsend discharge method, has recently found that γ_i for N_4^+ on Ni is of the order of 1 percent when corrected for back diffusion. This is, of the same order as that found in this study for nitrogen ions on Ta at the lowest ion energy.

O_2^+ and O^+ on O_2-Treated Ta and Pt

Figures 12 and 13 show the results obtained for a mixture of O_2^+ and O^+ ions incident on O_2-treated Ta and Pt, respectively. As was found for the nitrogen ions, the curves for oxygen ions on Ta and Pt lie fairly close to those for A^+ on O_2-treated Ta and Pt surfaces, respectively. Here again, this agreement is not unexpected as the energy available after neutralization of the oxygen ions is close to that for A^+. There is to be noticed for low-energy oxygen ions on Ta a slight increase of γ_i for decreasing ion energy; however, the effect is small compared with the similar effect found for nitrogen ions, and in this case its cause may well be instrumental.

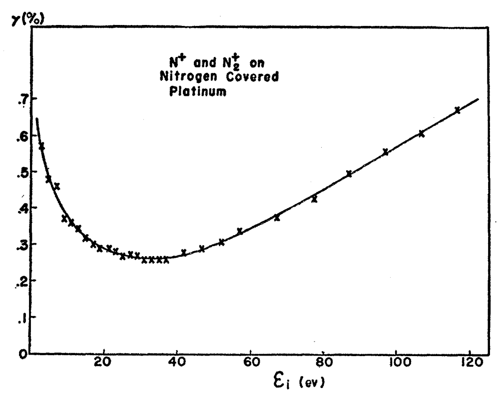

FIG. 11. Ejected electron yield (γ_i) for N_2^+ and N^+ ions on N_2-covered Pt. Here again γ_i increases at low energy.

H_2^+ and H^+ on H_2-Treated Pt

Figure 14 shows the results obtained for a mixture of the singly-charged hydrogen ions incident on H_2-treated Pt. This curve is seen to lie well below that for A^+ on H_2-treated Pt even though the energy after neutralization of the hydrogen ions is reasonably close to that of A^+. No study was made of γ_i for hydrogen ions on Ta.

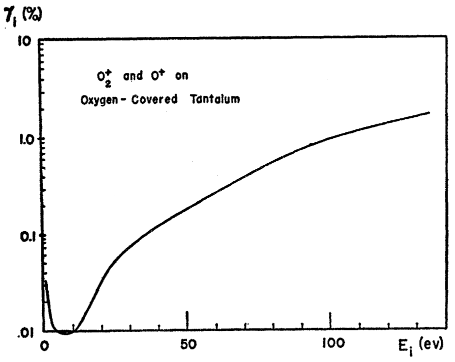

FIG. 12. Ejected electron yield (γ_i) for O_2^+ and O^+ ions on O_2-coated Ta. The increase in γ_i at low energies may be spurious here.

While there are no studies that can be directly compared with these results, still it is interesting to note the observations of Lauer[21] for H_2^+ on Ni using a pulsed Townsend discharge method of measurement with the pressure of H_2 ranging from 100 to 650 mm of Hg. While a photoelectric γ_p was obtained in Lauer's study which was of the order of 0.1 percent to 1 percent (corrected for back diffusion),[22] no positive ion γ_i was observed. Lauer estimated that γ_i had to be at least less than 10^{-4}. The very low γ_i observed in this study, was probably due to the thick H_2 films that form under high-pressure conditions.

IV. CONCLUSIONS

The theoretical interpretation of the γ_i process for slow positive ions incident on clean metals has been fairly clearly qualitatively described, but, as yet, is not on a quantitative basis. In principle the mechanism can best be pictured in terms of the schematic energy level diagram of Fig. 15. Here the levels of electrons in the metal and approaching ion are depicted as for

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[20] Elsa Huber, Phys. Rev. 92, 536 (1953).

[21] E. J. Lauer, J. Appl. Phys. 23, 300 (1952).

[22] J. K. Theobald, J. Appl. Phys. 24, 123 (1953).

infinite separation. Actually, as the ion approaches the metal its interaction with the metal alters the levels somewhat. It is seen that what happens is that an electron in the Fermi band is captured into the ground state of the ion and then another metallic electron is excited to an energy level above the Fermi band. The energy *available* to the excited electron depends on the region of the band from which the captured electron comes. Thus the available energies can range from $E_i - \phi$ for the upper limit and $E_i - W$ for the lower limit, where E_i is the ionization potential of the ion, ϕ is the work function, and W is the height of the surface barrier. On close approach the interaction energy decreases the available lower-limit energy, while the upper-limit available energy is unchanged. The method by which the effect of these interactions can be investigated has recently been independently developed by Hagstrum[11] and Varnerin.[12]

The process described above is termed the *direct* process originally proposed and treated by Shekhter.[9]

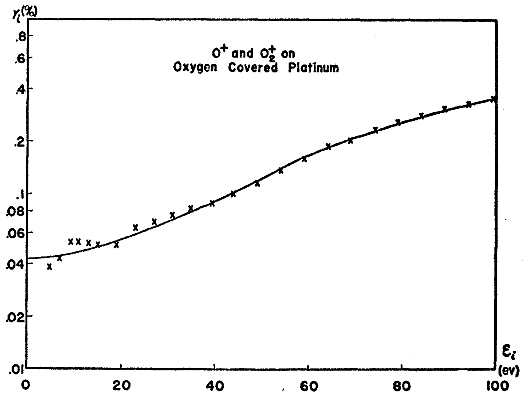

FIG. 13. Ejected electron yield (γ_i) for O_2^+ and O^+ ions on O_2-coated Pt.

Oliphant and Moon,[7] Massey,[8] and Cobas and Lamb[10] proposed and treated a two-stage process. In this the ion is first neutralized to an excited state by resonance capture of a metallic electron. From this state the atom subsequently decays to the ground state with excitation of a second metallic electron. The process active with A^+ ions is only the direct process since the values of ϕ for the surface used are greater than the difference between the lowest excited state and the ionization potential of A.

Now if part of the range of levels that may be occupied by the excited electron lies above the surface barrier, then those of the electrons in these levels that are directed toward the surface and are not reflected at the surface barrier are able to escape. The condition that the upper limit of the range of possible occupied levels lies above the surface barrier is that $E_i > 2\phi$.

It is seen, then, that if ϕ increases because of surface contamination the number of excited electrons in levels above the surface barrier will be less and thus γ_i will be decreased. It is thus essential to regard work functions and change in work function as gases are adsorbed. No work function data were obtained in these studies. However, Oatley,[23] and others, have found that H_2 *decreases* the work function of Pt slightly while O_2 increases ϕ by at least a volt. Weissler[24] has studied the changes in work function of surfaces of W and Ag after bombardment with hydrogen, nitrogen, and oxygen ions. Quite uniformly bombardment with A^+ or N_2^+ ions cleaned up the surface and restored the work function nearly to its normal value, while H_2 decreased the work function by a few tenths of a volt and O_2 increased it by the order of a volt or more. No data on Ta are available. On the other hand, Bosworth and Rideal[25] report that H_2, N_2, and O_2 films *all* increase the work function of W. Doubtless the conditions of formation and the nature of the films differed from those of Weissler and others. Accepting Oatley and Weissler's conclusion, it appears that there must be another action causing a reduction in γ_i beside that of an increase in ϕ. This is borne out by the following data. Hagstrum,[11] whose Ta was in the same state as that used here, observed a work function of 4.9 volts and

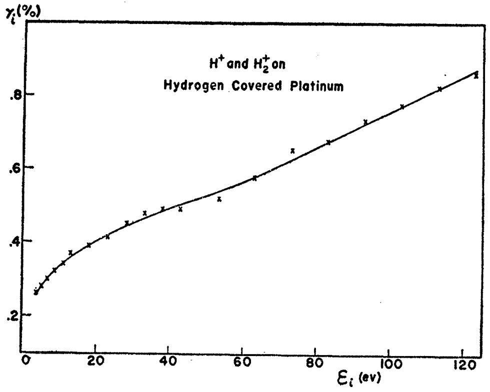

FIG. 14. Ejected electron yield (γ_i) for H_2^+ and H_2 on H_2-covered Pt.

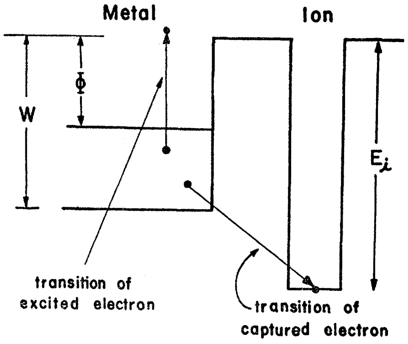

FIG. 15. Diagram showing the one-step mechanism of so-called potential electron liberation by positive-ion energy levels corresponding to infinite separation.

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[23] C. W. Oatley, Proc. Phys. Soc. (London), **51**, 318 (1939); A. L. Hughes and Dubridge, *Photoelectric Phenomena* (McGraw-Hill Book Company, Inc., New York, 1932).

[24] G. L. Weissler, J. Appl. Phys. **24**, 472 (1953).

[25] R. C. L. Bosworth and E. K. Rideal, Proc. Roy. Soc. (London) **A162**, 1 (1937); Proc. Cambridge Phil. Soc. **33**, 394 (1937).

the Ta had a gas film on it. As observed in this study, flashing the Pt target removed most of the active gas films so that the work function of the Pt used was not less than the accepted work functions of clean Pt of value 5.3 volts.[26] In consequence if the value of the work function alone determines γ_i the γ_i for Ta should be greater than that for Pt. Actually the reverse is true as noted. Again Hagstrum[11] observed that for He^+ ions on Mo after the background gas had formed a monolayer on the target γ_i was lowered by 30 percent while ϕ had not changed by more than 0.1 volt.

A guess as to the nature of this action comes from Hagstrum's observation that the energy distribution of electrons from the gas-covered surface had more slow electrons than that from the clean surface. This indicates that the probability of the excited electron occupying a low level in the range of levels available to it is greater for the gas covered surface than for the clean one. Such a condition would obviously also lower γ_i. The process active may be crudely envisioned as follows: with a clean surface neutralization involves direct interaction with only one electron of the Fermi band. With a covered surface it could well involve two for the electrons causing neutralization can come from a local state produced by an adsorbed gas atom. In general since such a local level does not lie in the Fermi band it will be refilled after neutralization by a metallic electron. Such a two-step process could well act to lower the energy available to the excited electron.

Thus gas coatings not only lower γ_i by raising ϕ, but also lower γ_i by reducing the *available* energy for excitation by a more complicated neutralization process. If the *lowering* of ϕ, for instance by H_2 treatment, is small the value of γ_i can still be decreased by H_2 films because of reduction of available escape energy. Likewise, clean Pt could yield a higher γ_i despite its 0.4-volt higher value of ϕ relatively to Ta, as Ta has a gas film at its surface.

That γ_i increases with ion energy is not surprising since kinetic liberation superposes on potential for all surfaces. For gas treated surfaces the observed increase of γ_i with energy is greater than for clean surfaces. This is to be expected for aside from some "cleanup" of the film by high-energy bombardment more of the high-energy ions penetrate the gas film and interact directly with metallic electrons; i.e., the interaction time with the local gas surface states is decreased relative to that with the lattice.

The initial decrease in γ_i with ion energy, observed *only* with nitrogen ions, can be accounted for by the very high energy of association of N atoms to form N_2 molecules. Thus in addition to the neutralization energy of N^+ ions these can react at the surface to yield N_2 at 9.6 ev and this energy may be available for electron liberation. Such a reaction may take place for slowly-moving low-energy ions and may decrease as ion energy increases.

In conclusion the writer wishes to express his appreciation for the support and encouragement given by Professor L. B. Loeb, who suggested this problem and under whose guidance it was carried out.

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[26] H. B. Michaelson, J. Appl. Phys. 21, 536 (1950).

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Liberation of Electrons by Positive-Ion Impact on the Cathode of a Pulsed Townsend Discharge Tube

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(Received December 7, 1953)

The parallel-plate Townsend discharge triggered by a flash of ultraviolet light on the cathode gives a current to the anode which depends strongly on the value of γ, the number of new electrons liberated from the cathode per positive-ion impact. An expression is derived relating γ to the first Townsend coefficient for ionization by electrons α and the anode-cathode separation X, which provides an easy experimental procedure for arriving at γ. Measurements are then given for γ as a function of E/p, the ratio of field strength to pressure, for Ne, A, and Kr on a freshly cleaned Mo cathode. The values of γ are essentially independent of E/p above 175 volts/(cm×mm Hg) with values of 0.20 for Ne^+, 0.083 for A^+, and 0.053 for Kr^+. At lower values of E/p, γ decreases toward zero, but this decline is probably related to the back diffusion of electrons to the cathode and does not represent a decrease in the basic γ process. With A^+ ions and a nickel cathode coated with activated $BaCO_3$, the value of γ also leveled off at higher E/p at a γ value related to the degree of activation of the $BaCO_3$. Significantly, the value of γ for this surface did not tend toward zero at zero E/p. This may be attributed to a different distribution of electron velocities for the ejected electrons from the coated surface than for the pure surface.

INTRODUCTION

THE emission of electrons from cathode surfaces as a result of positive-ion impacts has been studied for many years, first as an essential to the understanding of the mechanism of gas discharges and more recently as a challenging problem in the field of atomic interactions. Despite the number of years that the problem

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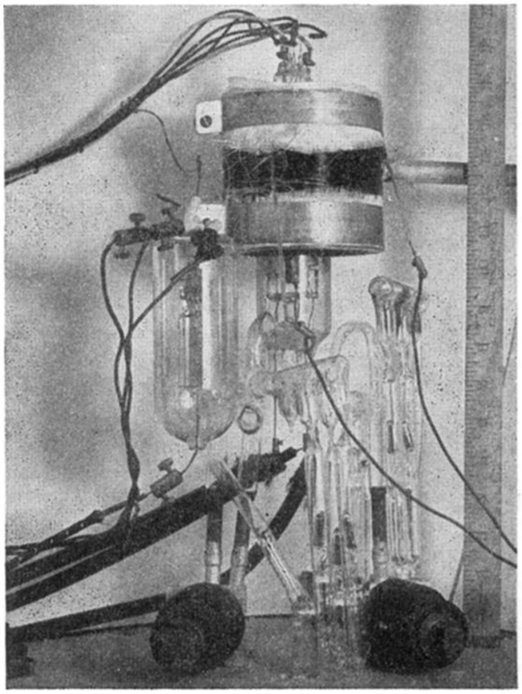

Fig. 6. The whole assembly showing vacuum techniques, and simplicity possible by Finkelstein-type source.