Charge Equilibrium Ratios for Hydrogen Ions from Solids*

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Experimental values for the ratios of the positive, neutral, and negative components have been obtained for proton beams in the energy region 3–200 kev emerging from Al, Be, Ca, Ag, Au, and SiO foils. Clean surfaces were obtained by evaporating fresh material onto the foil during a run. As expected, the equilibrium charge ratio appears to be determined by the last few ($\sim$5) atoms on the exit side of the foil. At 37 ± 3 kev, the positive and neutral components are equal for all materials tested, except Ca (18 ± 2 kev). Significant differences have been found in the charged components from these metals. The observed ratios of the components for different metals parallel their work functions at proton energies >100 kev.

INTRODUCTION

WHEN a beam of low-energy hydrogen ions passes through material, electrons are captured and lost by the ions, and particles of positive, neutral, and negative charge arise. A knowledge of such processes is important in the understanding of the slowing down of the ions by the material. Of interest are the ratios of the component intensities as a function of the ion energy and the dependence on the material through which the beam is passed.

A comprehensive review has been made by Allison and Warshaw[1] of the present knowledge of the charge exchange processes. To avoid repetition the reader is referred to this review for the considerable work done with proton beams passing through gases.

For the case of solids Hall[2] has measured the charged and neutral fractions of an equilibrated beam emergent from four metals in the energy range 20–400 kev. It was found that the equilibrium ratios produced in Be, Al, and Ag foils were the same. A slightly larger neutral component was obtained from the Au foil.

It has also been reported[3] that the charge ratios for helium ions emergent from solids is independent of the stopping material.

It has been suggested[1,2,4] that these results may be due to a surface layer of foreign material. The electron capture and loss cross sections are so large ($\sim 10^{-16}$ cm^2) that contaminating layers only a few atoms thick will completely alter the characteristic equilibrium ratio for the solid.

The present work was undertaken in an attempt to measure the equilibrium charge ratios for a surface as clean as practicable in the target area of an accelerator. Fresh material could be evaporated onto the exit side of the foil during an experiment and the rate of growth of the oxide and foreign material determined by changes in the charge ratios. Al, Be, Ca, Ag, Au, and SiO were evaporated in this manner. The negative component, which until that time was unknown in this energy range, was also measured.

APPARATUS

The apparatus is shown in Fig. 1. Analyzed protons of energy 5–250 kev from a Cockcroft-Walton accelerator passed through a thin aluminum foil. The emergent beam was collimated, magnetically analyzed into its charge components and detected by a phosphor-photomultiplier system. The charged components could be
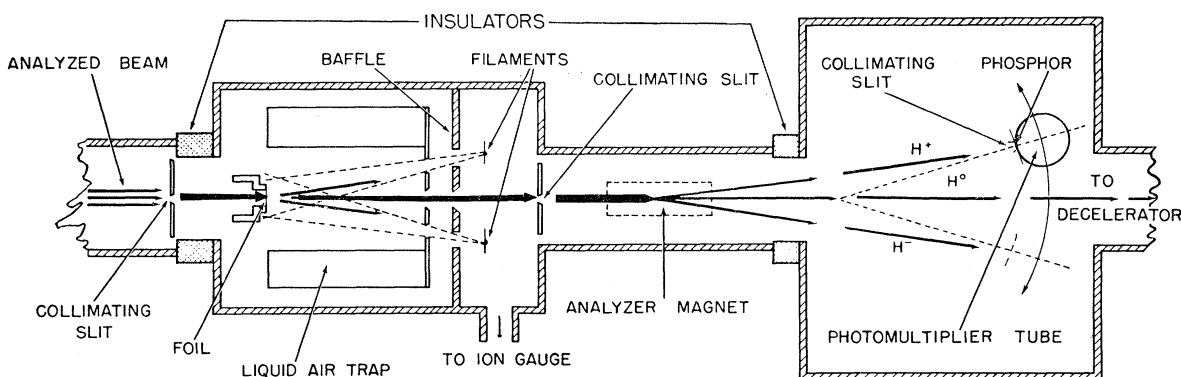

Fig. 1. Schematic diagram of the apparatus, showing the evaporator and detector.

[1] S. K. Allison and S. D. Warshaw, Revs. Modern Phys. **25**, 779 (1953).
[2] T. A. Hall, Phys. Rev. **79**, 504 (1950).
[3] G. Dissanaike, Phil. Mag. **357**, 1051 (1953).
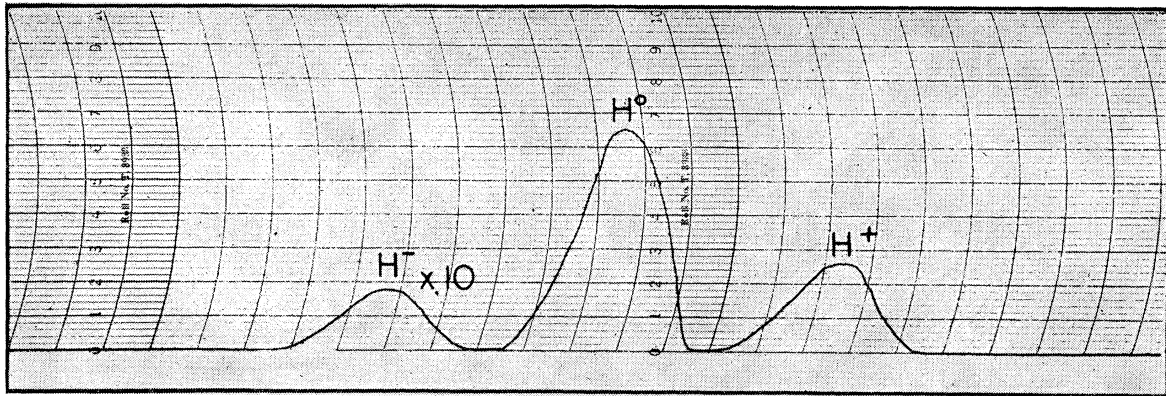[4] J. A. Phillips, Phys. Rev. **91**, 455(A) (1953).

FIG. 2. Record from the phosphor photomultiplier detector, showing the resolved charge components from a foil at an emergent proton energy of 20.5 kev.

sent into a decelerator by which the energy of the emergent beam was measured.

All the foils were of aluminum ($\sim$5-10 μg/cm^2) made by an evaporation technique.[5] The aluminum surface was always on the emergent side of the foil. Condensable matter in the vacuum was excluded from the exit side of the foil by providing liquid air cooled surfaces which surrounded it. Two evaporation filaments were provided by means of which layers of fresh material could be deposited onto the foil. Magnetically operated shutters made it possible to bring the filaments up to temperature before exposing them to the foils.

A 1P21 photomultiplier was mounted at the end of a rotating arm so that the detector could be swept through the three charge components. For complete separation of the three beams, the detector moved through an angle of $\pm$5°. As single particles were not counted but the integral effect of many ions was recorded, a fast phosphor was unnecessary and the phosphor was chosen for constancy under proton bombardment. Calcium tungstate was used with success and was coated onto a half-aluminized glass plate (to avoid charging up the phosphor) which in turn was mounted on the glass envelope of the photomultiplier. A narrow slit ($\sim$0.005 in. wide) was placed immediately in front of the phosphor at right angles to the motion of the detector. In this manner the beam, about 0.20 in. in diameter, would strike the same area of the phosphor as the detector was moved from one angle to another. A Brown recording milliammeter measured the output current of the photomultiplier after passing through an electrometer circuit. Records as shown in Fig. 2 were obtained as the detector automatically swept through the three charged components.

Several tests were necessary to show that the detector was satisfactory.

1. Linearity of detector response to beam current. Beam currents were varied by as much as 10^5; the

response of the tube was linear to better than 1 percent over this range.

2. Sensitivity as a function of the angle of the detector. With no foil in place, the analyzer magnet was varied to displace the beam from 0° to $\pm$15°. The response of the detector was constant ($\sim$1 percent) up to angles of $\pm$10° and increased thereafter. The components were never separated by more than 5° during the experiment.

3. As the axis of rotation of the detector was not located at the center of the analyzing magnet, it was convenient to show that the intensity of any charge component was proportional to the peak current as measured by the detector; see Fig. 2. Within 0.5 percent, the areas under the current curves were proportional to the peak currents if the detector was not moved through angles greater than $\pm$5°.

4. The total beam was equal to the sum of its components. The response of the phosphor is considered to be identical for the positive, neutral, and negative components of the beam. The charge exchange cross sections are so large that as soon as an ion has traversed the first few atoms of the phosphor it has completely lost its initial identity. The total beam and its three components could be measured separately and within 1 percent the sum was equal to the total unresolved beam.

5. Light produced by the beam passing through the residual gas in the vacuum chamber could be detected by the phosphor. The only response of the detector (when a glass plate was placed immediately in front of the detector) was from the fluorescence of the glass by the beam and was a thousand times smaller than with the same beam current on the phosphor.

6. The distance of the analyzer magnet from the foil was 20 cm and it was important that no appreciable charge exchange should occur in this region. The pressure was increased from 5$\times$10^{-6} mm Hg to 10^{-4} mm Hg and no change in the charge ratio greater than 1 percent was observed.

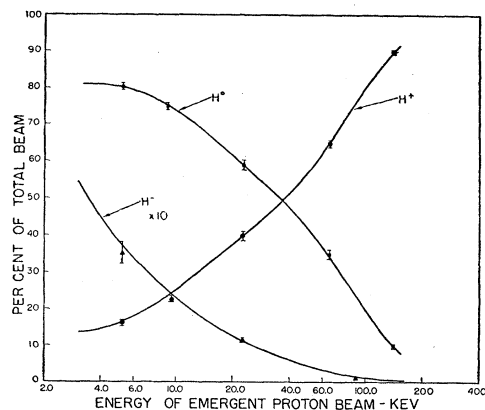[5] G. A. Sawyer, Rev. Sci. Instr. 23, 604 (1952).

FIG. 3. Equilibrium proton charge ratios from an aluminum foil contaminated with foreign material on its surfaces as a function of exit energy. (Several experimental points are included to show the probable error.)

RESULTS

With an aluminum foil in place, the relative intensities of the three charged components were measured several times at each energy; see Fig. 2. The beam diameter was 3 mm and currents of 0.001–0.3 μa were used, the larger currents being necessary at low beam
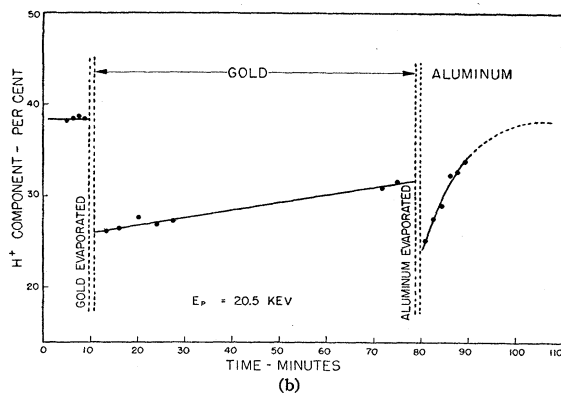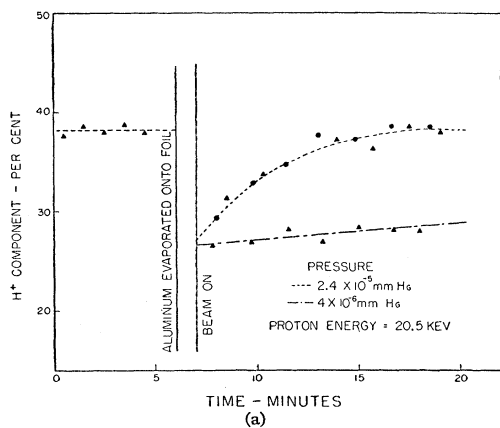

TIME – MINUTES
(a)

TIME – MINUTES
(b)

FIG. 4. Changes in the amount of the H^+ component as a function of time as (a) aluminum is evaporated onto the foil, and (b) gold and then aluminum are evaporated under identical conditions.

energies where scattering in the foil and low sensitivity of the detector became serious. Lower equivalent proton energies were obtained by the use of deuterons and tritons as the incident particle.[6] The energy lost by the beam in the foil (4–7 kev) was measured with the decelerator[7] and the emergent energy of the beam from the foil could be calculated to within 50 ev.

All newly installed foils, and foils which had been in the apparatus for some time, gave equilibrium ratios as shown in Fig. 3. As expected, at high proton energies the positive component was the largest and as the energy decreased the neutral and negative components increased. The positive and neutral components were equal at a proton energy of 37±3 kev. At 3.2 kev, the lowest energy examined, the negative component (~5.5 percent) was still smaller than the positive component (~13 percent). The constancy of these ratios for untreated foils was used as a check on the apparatus before each run.

When fresh material was evaporated onto the exit side of the foil the following effects were noted with each metal.

Aluminum

Immediately after the evaporation of a layer of aluminum the ratios were found to have changed as shown in Fig. 4(a). In this case, with a beam energy of 20.5 kev, the H^+ component was found to have changed immediately after the evaporation from 38 percent to 26 percent. The H^+ component was then found to increase and come back to its original value. Decreasing the pressure by a factor of 6 increased this time by about the same factor.

It is thought that initially the surface has a layer of foreign material which gives the 38 percent H^+ component. The new value of the H^+ component (26 percent) immediately after evaporation is due to the fresh aluminum layer on the surface which subsequently either oxidizes in residual air in the vacuum or is covered by a layer of dirt resulting in the initial 38 percent H^+ component. The two possibilities, oxidation or accumulation of dirt, were separated by depositing first a layer of gold followed later by a layer of aluminum under the same conditions. The results are shown in Fig. 4(b). Gold, which does not oxidize appreciably, took several minutes to return to the initial condition, whereas aluminum which does oxidize was relatively much faster. It is concluded that the rapid change of aluminum is due to the process of oxidation and the slow change of gold is due to the growth of a dirt layer.

Some effort was made to measure that thickness of the evaporated aluminum layer in which charge-exchange equilibrium will be reached. It was found that a layer about 50 ev (or 6 atoms) thick is sufficient for equilibrium. It is not known how significant this meas-

[6] J. A. Phillips, Phys. Rev. 90, 533 (1953).
[7] Arnold, Phillips, Sawyer, Stovall, and Tuck, Phys. Rev. 93, 483 (1954).

urement might be, since at these temperatures the aluminum atoms have mobility and may aggregate into crystals. For this reason it is considered unprofitable to determine more precisely this minimum equilibrium thickness since an area and not a thickness effect might be measured. During the experiment layers of at least five times this thickness were deposited.

It is of course impossible to state definitely that the data, when extrapolated back to the time when the evaporation has been completed, are those for aluminum. Changes (to the aluminum) may have occurred during the evaporation process and the transport of the metal to the foil. Moreover, sixteen seconds elapsed after an evaporation before a measurement of the charge ratios could be made. This possibility is thought, however, to be unlikely, as the extrapolations of data taken with pressures differing by a factor of 6 agree within the experimental error.
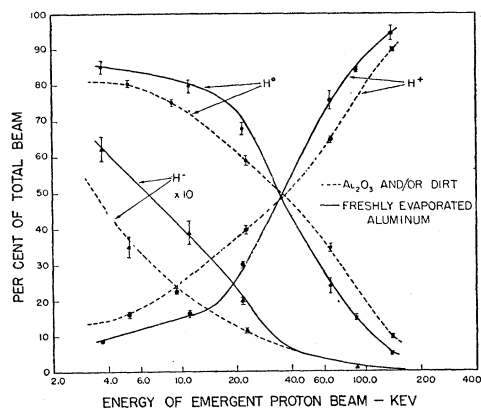

FIG. 5. Comparison of the equilibrium charge ratios from a freshly evaporated aluminum surface with a "dirty" surface.

Evaporating aluminum at several proton energies and extrapolating to zero time, the ratios for aluminum were found as shown in Fig. 5. A few of the experimental points are included to show the probable error.

Beryllium

Beryllium was evaporated from tantalum filaments and found to be very similar in behavior to aluminum. The rate of growth of the oxide made it necessary to evaporate fresh material onto the foil at each energy and to extrapolate the data to zero time.

Silver, Gold, and SiO

The equilibrium ratios could be measured at several energies before the growth of contaminating layers of dirt became serious. The condition of the foil was constantly monitored by repeatedly returning to that energy first used after an evaporation.
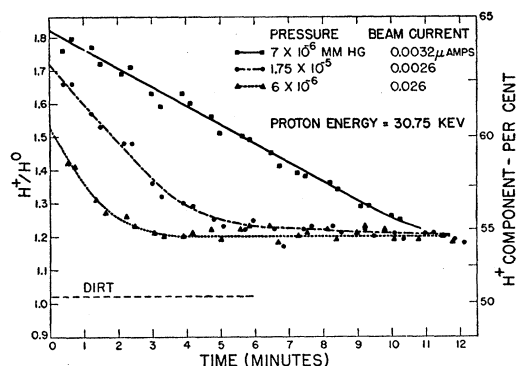

FIG. 6. Changes in the H^+ component from calcium as a function of time under different beam and vacuum conditions.

Calcium

Considerable difficulty was experienced with the high chemical reactivity of this metal. Not only did the metal react quickly on the foil, but the metal reacted while on the evaporating filaments, making it increasingly difficult to evaporate it during a run. Both the vacuum pressure and the magnitude of the beam current through the foil were found to change the rate of growth of the oxide, as shown in Fig. 6. Such data show that at the lowest pressures ($\sim 5 \times 10^{-6}$ mm Hg) and the smallest beam currents (~ 0.001 μa) used in the experiment the surface had probably changed before a measurement of the charge components could be made. The results given for calcium are extrapolations of the data taken under the most favorable conditions but are probably contaminated to some extent.

The results for the metals examined in this experiment are shown in Figs. 7 and 8, and numerical values in Table I.
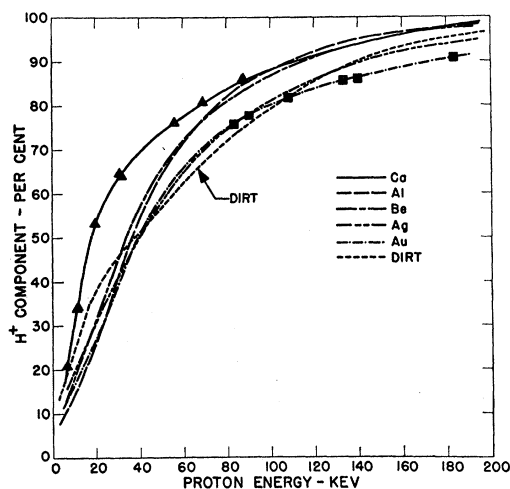

FIG. 7. H^+ component from several metals as a function of emergent proton energy.
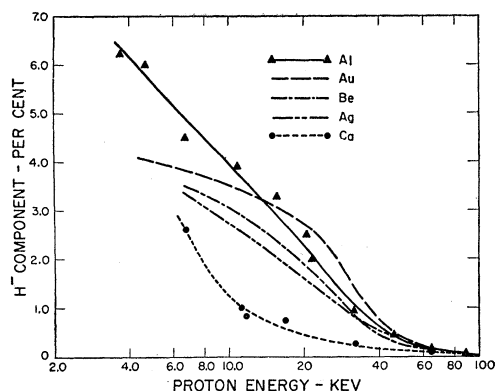
FIG. 8. H⁻ component from several metals as a function of emergent proton energy.

DISCUSSION OF RESULTS

1. The above data indicate that contrary to earlier investigations there are variations in the proton equilibrium charge ratios from metals. It appears likely that the previous results were due to layers of foreign material on the foil masking the ratio from the metal. The large discrepancies between observers could then be explained by the use of different pump oils, methods of trapping, and other contaminants.

2. In the present experiment only the ratios of the components of the emergent beam were measured and not the capture (σ_c) and loss (σ_l) cross sections. It can be shown that if equilibrium has been obtained and the negative component is negligible,

$$f_+/f_0 = \sigma_l/\sigma_c,$$

where f_+ and f_0 are the fractions of the beam which are positive and neutral respectively.

It has been predicted[8] that the loss and capture cross sections should be proportional to some power (n) of
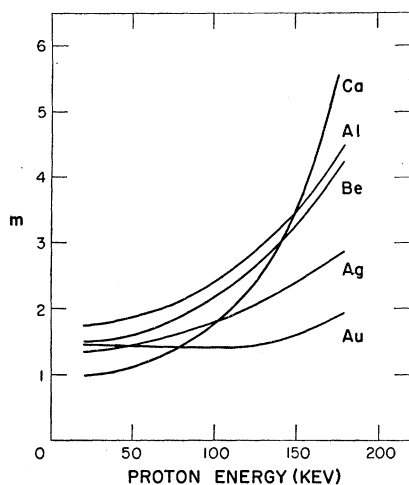

FIG. 9. Exponent m for the energy dependence of the ratio f_+/f_0.

[8] L. H. Thomas, Proc. Roy. Soc. (London) 114, 561 (1927); H. C. Brinkman and H. A. Kramers, Proc. Acad. Sci. Amsterdam 33, 973 (1930); N. Bohr, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. 18, No. 8, 144 (1948).

the particle velocity and dependent on the atomic number of the material when the velocity is much larger than $v_0 = e^2/\hbar$, the velocity of the hydrogen orbital electron. A summary for several cases is presented in Table II.

Applying these concepts to the present experiment, the measured ratio will take the form

$$f_+/f_0 = \sigma_l/\sigma_c = kE^m,$$

where E is the energy of the particle. For light elements m should take values between 3 and 6 and for heavy elements about 3. In Fig. 9 the calculated values of m as a function of energy are shown.

In general the experimental results are in agreement with the theory. For the light elements, Be and Al,

TABLE I. Percent of positive, neutral, and negative components of a proton beam from several elements.

Element	Energy—kev							
	4.0	7.0	10.0	20	50	100	150	190
Dirt								
H⁺	14.5%	19.7%	25.0%	37.6%	57.0%	79.9%	91.2%	96.0%
H⁰	81.0	77.3	72.7	61.2	42.5	20.0	8.8	4.0
H⁻	4.5	3.0	2.3	1.25	0.46	0.10	0.02	...
Aluminum								
H⁺	8.2	11.2	14.2	25.1	64.0	87.9	95.5	98.2
H⁰	85.6	84.0	81.8	72.5	35.6	12.0	4.5	1.8
H⁻	6.2	4.8	4.0	2.4	0.37	0.06	0.04	...
Beryllium								
H⁺	...	13.7	17.6	31.0	65.6	86.6	95.2	97.8
H⁰	...	82.8	79.3	67.1	34.1	13.4	4.8	2.2
H⁻	...	3.5	3.1	1.9	0.27	...	...	...
Calcium								
H⁺	...	17.5	30.4	53.3	73.7	88.3	95.0	98.5
H⁰	...	80.1	68.3	46.2	26.2	11.7	5.0	1.5
H⁻	...	2.4	1.3	0.48	0.13	...	...	...
Gold								
H⁺	10.2	13.2	16.5	26.7	59.5	80.4	87.6	91.5
H⁰	85.6	83.0	80.0	70.5	40.1	19.5	13.4	8.5
H⁻	4.2	3.8	3.5	2.8	0.4	0.09	0.05	...
Silver								
H⁺	...	15.9	19.3	30.1	58.3	81.5	91.2	94.5
H⁰	...	80.8	78.0	68.2	41.4	18.4	8.8	5.5
H⁻	...	3.3	2.8	1.7	0.27	0.07	0.02	...
SiO								
H⁺	...	20.0	24.7	36.8	59.8	83.9	92.4	...
H⁰	...	77.1	73.0	61.9	39.8	16.0	7.6	...
H⁻	...	2.9	2.3	1.3	0.41	0.06	0.04	...

the values of m for high velocities are large ($\sim$4–5) and for the heavier elements, Ag and Au, m is almost constant over the velocity range examined and has a value of $\sim$2.

3. The negative components decrease rapidly with increasing energy and at 150 kev are less than 0.1 percent of the total emergent beam. For the metals examined, those which have the largest neutral component at low energies (Al and Au) also have the largest negative components. In Fig. 10 is shown the ratio f_-/f_0 as a function of energy, where f_- is the fraction of the beam which is negatively charged. This ratio f_-/f_0 is also equal to the ratio of the capture and loss cross sections of the second electron if double electron loss and capture are neglected. The slopes of these curves for Al, Be, Ag, and Au have the values -0.3 ± 0.2 at low energy and -1.8 ± 0.3 at high energies. The slope

for Ca is constant in this energy range and has a value of -0.9 ± 0.2.

Freshly evaporated Al gave the largest negative component which was 6 percent at 3 kev. At this energy, with a beam of 5 μa (limited by the foil), it is then possible to obtain a negative hydrogen beam of about 0.3 μa.

4. As the hydrogen particles leave the metal, the effect of the surface layer on the charge ratios is unknown. Oliphant and Moon,[9] Cobas and Lamb,[10] Varnerin,[11] and others have considered a similar problem for the scattering of helium ions from surfaces and the creation of the helium metastable state. It might then be expected that the charge ratios inside the metal are changed by some process dependent on a characteristic of the surface, e.g., the work function. In Fig. 11, are plotted the H^+ components against the work function of the metals at several energies. A surprisingly good correlation is found for energies above 100 kev if the value of 4.41 ev[12] be taken as the work function for evaporated Ag.

DISCUSSION OF ERRORS

As the charge ratios are determined by the last few atomic layers the results will be meaningful only if fresh clean surfaces have been used. It is not known

TABLE II. Exponents for the velocity dependence of $\sigma_l \propto v^{n_l}$ and $\sigma_c \propto v^{n_c}$.

Elements	n_l	n_c
Light	-2 ⎫	-5.5 to -12
Intermediate	-1 ⎬	
Heavy	0	-6

absolutely whether, in the few seconds (~16) between an evaporation and a ratio determination, changes have occurred. The results of several tests (e.g., increasing the vacuum pressure, varying the beam current and layer thickness) indicate that if changes have taken place in this time interval they are small (<2 percent). As stated above, the calcium ratios are the most inaccurate due to the great chemical reactivity of calcium and the resulting difficulty in extrapolating to zero time.

Random errors are small; beam component determinations, detector sensitivity, and thickness of the foil together contribute about 3 percent to the error.

SURFACE EFFECTS

The mechanism proposed by Oliphant, Moon et al.,[9–11] for the ionization and neutralization of the helium atom in the field of the surface of a metal may be applicable

[9] M. L. E. Oliphant and P. B. Moon, Proc. Roy. Soc. (London) A127, 388 (1930).
[10] A. Cobas and W. E. Lamb, Phys. Rev. 65, 327 (1944).
[11] L. J. Varnerin, Jr., Phys. Rev. 91, 859 (1953).
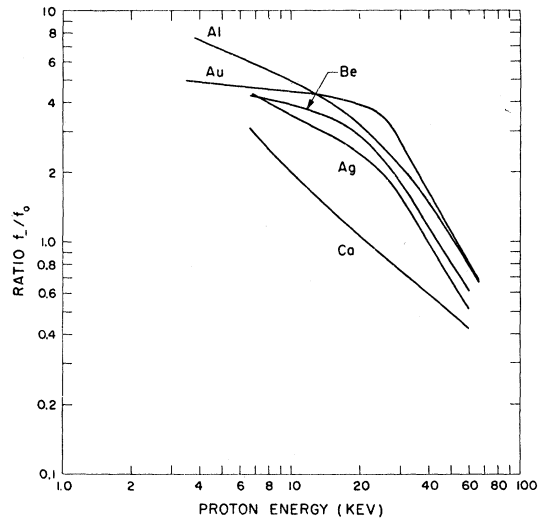[12] L. L. Blackmer and H. E. Farnsworth, Phys. Rev. 77, 826 (1950).

FIG. 10. Ratio f_-/f_0 as a function of energy.

to protons. The magnitude of such a surface effect if it occurs might be measured by keeping the charge ratio in the interior of the metal constant, i.e., the emergent beam energy constant, and varying the time the particle remains in the field of the surface. This can be done by varying the inclination of the foil to the beam while making appropriate adjustments to the beam energy.

The region of the surface which is of interest is small: ~3 A thick. Thus to observe any effect as proposed the surface must be smooth and as free as possible from crystal structures. An amorphous surface as SiO should be ideal.

In Fig. 12, the energy loss of a 50-kev incident beam of protons passing through an inclinable foil is compared with a calculated curve assuming a $\Delta E \propto \sec\theta$ dependence and correcting for the variation of $\Delta E/\Delta x$ with energy. The good agreement (~3 percent) indicates that foils made by such an evaporation technique are uniform and that the energy lost by the beam in a foil can be calculated from the angle of inclination and the
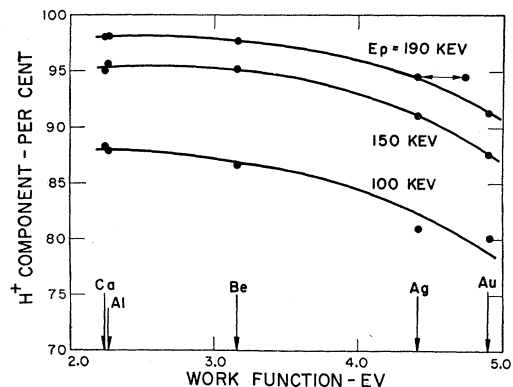

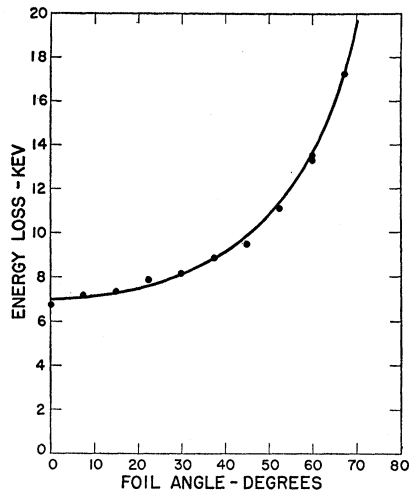FIG. 11. H^+ components as a function of the work function of the metals at several energies.

FIG. 12. Energy loss of an incident 50-kev deuteron beam in a foil as a function of the angle of the foil.

FIG. 13. Variation of the H^+ component as a function of the angle of the foil. (The dotted line is the H^+ component from a foil normal to the beam direction in which the emergent beam energy was varied.)

measured energy loss in the foil when the beam is normal to the foil.

When the H^+ component is measured from a dirty aluminum foil at different emergent energies by keeping the incident energy (50 kev) constant and varying the angle of inclination, the results shown in Fig. 13 are obtained. The dotted curve is the H^+ component from a similar foil normal to the beam direction as the emergent energy is varied by changing the incident beam energy on the foil. No effect within the experimental error ($\sim$2 percent) is found when the foil is inclined. This negative result is not conclusive in that it is known that impurities tend to condense preferentially onto a surface. The resulting rough surface would not be expected to show an effect when the foil angle is changed.

In order to obtain as flat a surface layer as possible, fresh layers of SiO and Au have been evaporated normally onto an inclinable foil during the experiment. If the beam were left normal to the foil the charge ratios would have remained relatively constant (after the initial charge following the evaporation) except for the slow growth of foreign material onto the surface as shown in Fig. 4(b). However, when the foil angle is changed the charge ratios varied with time in as yet an unpredictable manner. Though this variation in the charge ratios was small, e.g., at 50-kev incident proton energy a 6 percent change in the H^+ component has
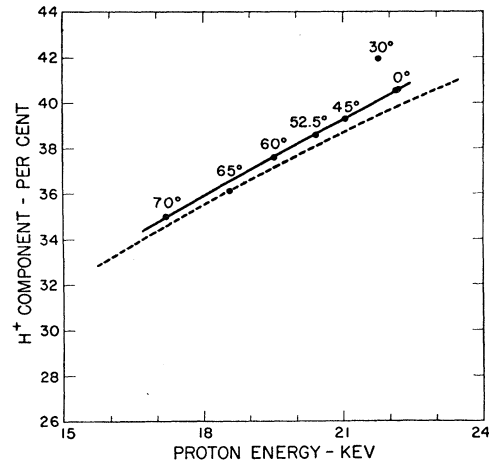
been observed, the effect was such that it overshadowed any systematic variation with angle.

CONCLUSIONS

From the evidence obtained in this experiment the following conclusions are drawn.

1. The charge ratios of a proton beam emergent from a metal surface in the energy range 3–200 kev are determined by the last few atomic layers of the material and the emergent energy of the beam.

2. The charge ratios from Ca, Al, Be, Ag, and Au are different in this energy range.

3. Above a proton energy of 100 kev there is a correlation between the charge ratios and the work function of the metal.

4. When the surface of a dirty foil is inclined at different angles to the beam direction, the charge ratios are the same as with a normal foil at the same emergent energy. Small unpredictable changes ($\sim$6 percent) are found with fresh SiO and Au when the foil is inclined.
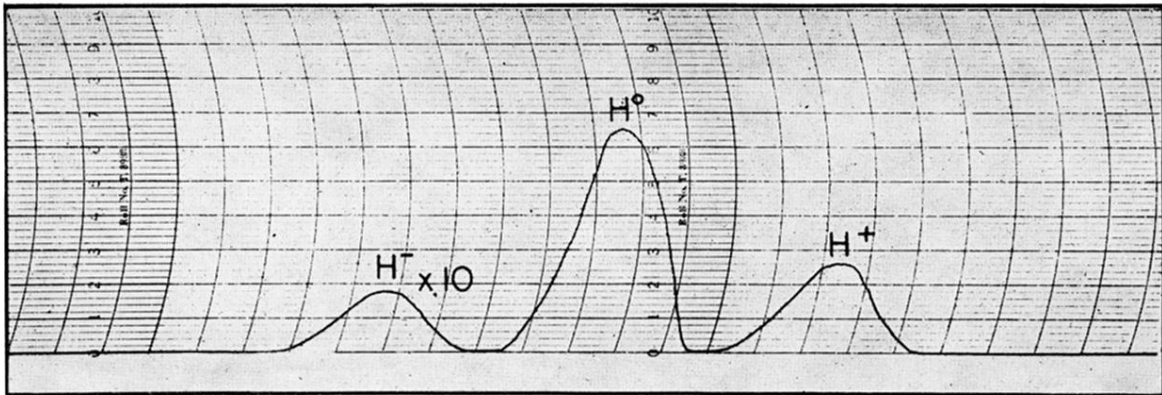
ACKNOWLEDGMENT

FIG. 2. Record from the phosphor photomultiplier detector, showing the resolved charge components from a foil at an emergent proton energy of 20.5 kev.