view. The band at about 3·3 μ characteristic of the aliphatic C-H linkage, which usually consists of several components in the higher members, gives place to a single line in chloroform and bromoform.

From a comparison of the data it appears that the Raman line corresponding to $\Delta\nu$ 750 can be ascribed to a vibration in the C-Cl bond, whereas the one corresponding to $\Delta\nu$ 660 can be ascribed to the C-Br bond. The diffuse nature characterising the Raman lines shifted by the above frequencies, which is particularly conspicuous in $CHCl_3$, CCl_4, and $CHBr_3$, may be due to an unresolved structure arising from the presence of isotopes in chlorine and bromine.

In conclusion, the authors desire to express their best thanks to Prof. Sir C. V. Raman, F.R.S., and Mr. K. S. Krishnan for their kind interest in the work. The investigation was carried out in the laboratory of the Indian Association for the Cultivation of Science.

The Liberation of Electrons from Metal Surfaces by Positive Ions. Part I.—*Experimental.*

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Modern theories* of the glow and arc discharges require that electrons should be set free from the cathode surface as a result of the bombardment by positive ions. The conditions in the neighbourhood of the negative electrode are exceedingly complex, and it is only by systematic examination of each reaction which we believe to be present, isolated from the disturbing effects of the others, that we can hope for a complete understanding of this important region. This paper describes some experiments which have been carried out in an endeavour to explain the precise nature of the reaction between the positive ions and the surface of the conductor.

The literature of this subject is fairly extensive, and many of the experiments

* *Cf.* Compton and Morse, 'Phys. Rev.,' vol. 30, p. 305 (1927).

have been very carefully thought out.* It seems to be quite definitely established that ions of velocity greater than about 100 volts set free electrons from metal surfaces which are not rigorously freed from gas. Most of the experiments have been carried out with alkali ions from thermionic sources, and owing to the abnormally low ionisation potentials of the alkalis the results are scarcely applicable to the case of discharges in ordinary gas. We are not concerned with the liberation of electrons by very fast canal rays or alpha particles, but with the effect produced by positive ions of less than about 1000 volts energy. Penning† has established by a series of experiments that neon ions of as little as 7 volts energy, drifting up against a metal surface, are able to set free electrons from it.

The present experiments were carried out with helium ions, except in one or two special instances, for three reasons. Firstly, the part played by the ionisation potential will probably appear very clearly with a gas of such high ionising energy; secondly, it will not be adsorbed appreciably at the surface of the conductor, and after neutralisation will escape again in the atomic condition; while thirdly, it can be continually and easily purified by passing over activated charcoal cooled in liquid air.

Two methods of examining the emitted electrons have been employed. The most careful experiments have been carried out by a retarding potential method, but these results have been confirmed by experiments using magnetic analysis of the velocity distribution.

Apparatus.

The production of a homogeneous beam of gas ions is by no means as simple as in the case of the alkali ions, for a thermionic source does not exist, but a method has been developed, based on the Langmuir "probe" theory, which yields a beam surprisingly "monochromatic" in character and of fair intensity.

It is known from the work of Langmuir and Mott-Smith,‡ that a negatively charged electrode in a strongly ionised gas becomes surrounded by a sheath of positive ions, whose space charge neutralises the potential of the electrode at points outside the sheath. Every positive ion which crosses the outer boundary of this dark sheath must eventually reach the electrode, unless it makes a collision in its passage across the space, or the electrode is so small

* 'Handbuch d. Physik,' vol. 24, p. 171, *et seq.*

† Penning, 'K. Akad. Wet. Amsterdam, Proc.,' vol. 31, p. 14 (1927); 'Physica, vol. 8, p. 13 (1928).

‡ Langmuir and Mott-Smith, 'Gen. Elec. Rev.,' vol. 27, p. 449 (1924).

that the random ion velocities are able to cause it merely to perform an orbit about the probe. If the ionised gas is the positive column of a glow discharge or a low voltage arc, the random velocities of the ions will be only of the order of a few volts, so that after traversing the sheath the greater number will strike the electrode with the energy corresponding to its potential relative to the surrounding gas. The abnormally long free paths of ions in most gases support the probability that there is little loss of energy by the ions in traversing a sheath which is not too many gas-kinetic free paths in thickness. If the electrode is perforated in such a way that the field is not seriously distorted, that is, so that the diameter of the perforations is small compared with the sheath thickness, ions will travel through with a velocity determined only by the potential applied. These facts have been utilised in the method employed for producing a beam of He^+ ions.

Helium gas was admitted to the bulb O, fig. 1, through a fine leak, passing on the way over activated charcoal cooled in liquid air. An arc of 50-400

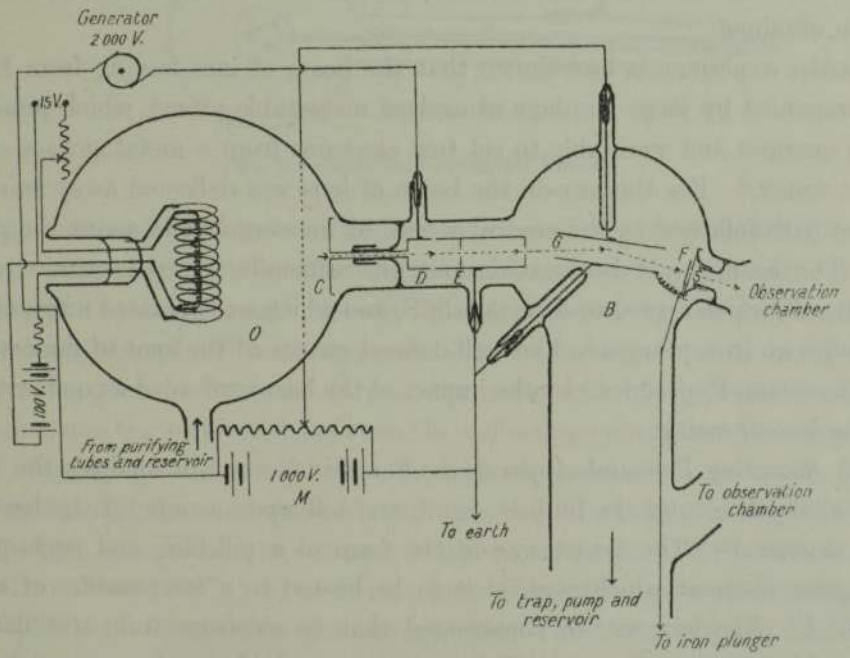

FIG. 1.—Apparatus for the Production of a Homogeneous Beam of Gaseous Ions.

milliamperes at 100 volts was maintained in O between the tungsten filament and the neighbouring grid. The gas was thus highly ionised, and when a negative potential was applied to the plate C, immersed in the gas, it attracted positive ions, building up round itself a protective space-charge sheath sharply

defined as a dark space about 1 cm. thick. Between the edge of the dark space and C the ions were accelerated by the full potential of C relative to the gas around it, that is, practically the potential of this electrode relative to the anode of the arc. Some few of these ions entered the hole in the centre of the electrode. Of these the larger portion collided with the walls of the canal, 3 mm. in diameter and 5 cm. long, but a few travelled right through. Between D and E these ions were subjected to a reversed field, due to the potential between the anode of the arc and C applied in the opposite direction, but diminished by a battery of small storage cells M. In this way a beam of ions was obtained whose energy was independent of the high potential from the generator applied to C in order to collect them from the glowing gas. It was not possible to vary the " pulling out " potential in order to change the energy of the beam of ions. A potential of at least 1500 volts was required on C, as at lower potentials the thickness of the positive ion space-charge sheath was so small that the hole in the centre of the electrode caused a serious disturbance of the field, and a resultant decrease in the intensity of the beam obtained.

Earlier experiments had shown that the beam of ions issuing from E was accompanied by large numbers of excited metastable atoms, which possessed high energies and were able to set free electrons from a metal surface which they struck.* For this reason the beam of ions was deflected away from the direct path followed by the neutral atoms, by an electric field across the plates G. The beam could be located upon the willemite covered surface of the shutter F, which served to close the slit S, and which was operated magnetically through an iron plunger. The well-defined nature of the spot of fluorescence on the screen F, produced by the impact of the beam, afforded a good criterion of its homogeneity.

(*a*) *Retarding Potential Apparatus.*—For this method of analysis the beam was allowed to enter the bulb D, fig. 2, and fall upon a target T, by lowering the shutter F. The target was in the form of a pill-box, and contained a tungsten filament which enabled it to be heated to a temperature of about 1200° C. The box was so constructed that no electrons from the filament were able to escape from it. The target was carried on a long ground glass joint, cooled by a stream of water flowing through a coil of metal tubing cemented to the outer sleeve. In this way the whole of the glass portions of the apparatus, right up to W, could be baked out at 550° C. The bulb was covered with a conducting film of platinum, deposited in a vacuum

* Oliphant, ' Roy. Soc. Proc.,' A, vol. 124, p. 228 (1929).

by evaporation from a heated wire, contact being made by wires sealed through the wall of the bulb. A variable retarding or accelerating potential could be

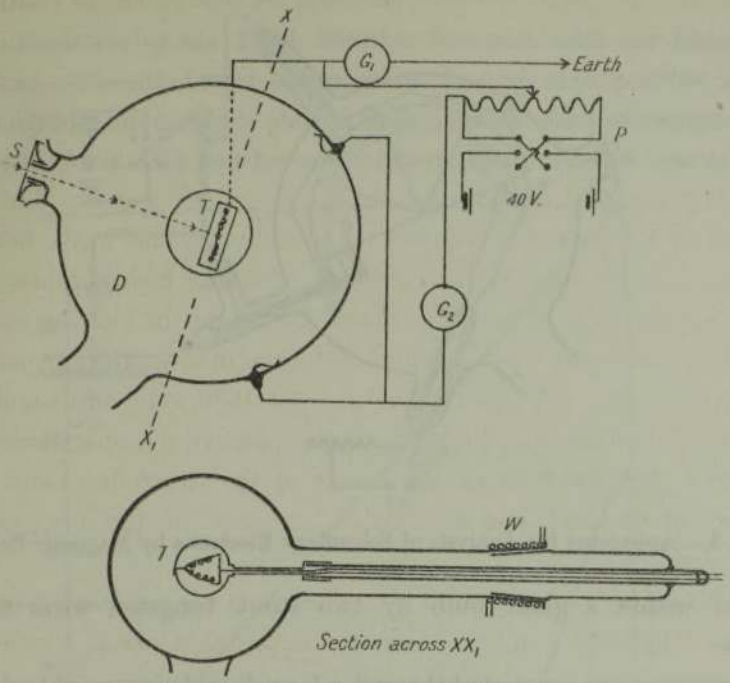

FIG. 2.—Retarding Potential Effects.

applied between the target and bulb by means of a potentiometer P. The current to the target and the collecting sphere, *i.e.*, the total positive ion current entering the system through the slit S, was measured by the galvanometer G_1, and varied up to 45 microamperes. The secondary electron, or reflected positive ion current from the target, was measured by the more sensitive galvanometer G_2, connected between the collecting sphere and the target.

(*b*) *Magnetic Analysis.*—For this method of observation the beam, after passing through the slit behind the shutter, was directed upon the target T, fig. 3, which was inclined at an angle of 45° to the beam, and which could be heated to about 1200° C. by radiation from a coiled tungsten filament inside the "pill-box" attached to the opposite face. Electrons set free from this target were bent into a semicircle by the field of a pair of Helmholtz coils, the beam being defined by the usual slit system. The final slit was 0·25 mm. wide and 4 mm. long, and below it was fastened the Faraday cylinder Z, insulated with quartz, and surrounded by an insulated guard ring Q, the whole being enclosed in a shielding box U. The complete system of target, slit system and shielding box was cut and folded from a single sheet of molybdenum,

to eliminate contact potentials, and the Faraday box was rolled from the same piece. All joints were lapped and spot welded. The analysing apparatus was

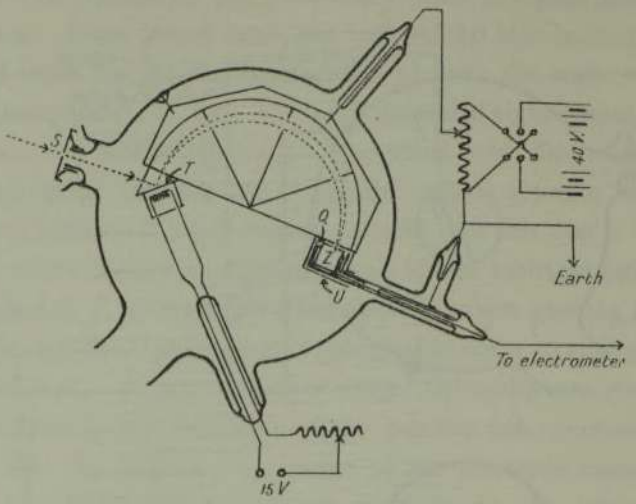

Fig. 3.—Apparatus for Analysis of Secondary Electrons by Magnetic Bending.

suspended within a glass bulb by two stout tungsten wires sealed into the walls.

The apparatus was evacuated through a large liquid air trap of low resistance, by a four-stage Gaede diffusion pump, which returned the helium gas to the reservoir. The pressure on this side of the canal was maintained at less than 4×10^{-5} mm. with a pressure of 0·01 mm. in O, fig. 1. An auxiliary pumping system allowed the whole apparatus, reservoir and Gaede pump, to be evacuated and the glass parts baked out till the residual pressure was not greater than 10^{-6} mm. as measured by an ionisation gauge. The system was separated from the exhausting pump and gas inlet by mercury cut-offs, barometrically operated. The helium used was purified by fractionating 10 times from charcoal in liquid air, slight traces of hydrogen being removed by electrolysing a trace of oxygen from the glass wall of a discharge tube into the glowing gas, after a method described by Taylor.*

The whole apparatus was of pyrex glass with tungsten seals, the metal parts molybdenum or nickel, with the exception of the canal and the coating on the collecting sphere, which were of platinum. The ground joints at W, fig. 2, and those on the steel Gaede pump, were lubricated with a grease of very low vapour pressure.†

* ' Roy. Soc. Proc.,' A, vol. 123, p. 252 (1929).

† Burch, ' Roy. Soc. Proc.,' A, vol. 123, p. 271 (1929).

The system of electrical connections used is shown in the figures, and does not call for comment.

Results.

(*a*) *The Variation of the Total Electron Emission with the Energy of the Positive Ions.*—The number of electrons set free by each positive ion which struck a molybdenum target is plotted in fig. 4 for a series of energies from 80 to 1000 volts, for a cold and for a red hot surface. In the case of the cold

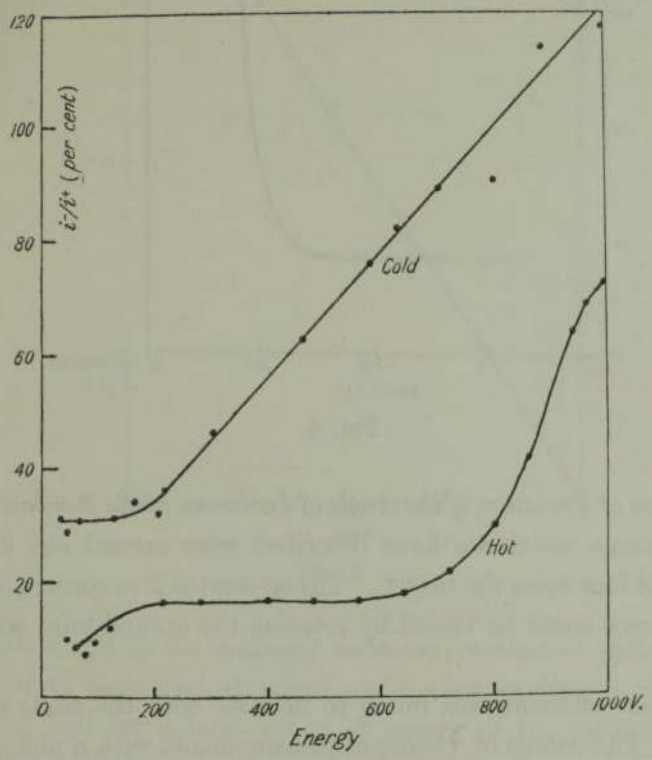

Fig. 4.

target the points do not lie on a smooth curve, although they give a fairly accurate idea of its general shape. The emission was reasonably constant at energies below about 200 volts, but beyond this point it increased approximately linearly with the energy up to 1000 volts. When the target had been heated for some time at a bright red heat, and was maintained red hot during the measurements, the curve obtained was very much smoother, and was reproducible. The emission did not now begin to increase till a potential of about 500 volts was reached, when it increased gradually, assuming an approximately linear form beyond 800 volts, but curving over again beyond 1000 volts. The emissions were also smaller than with a cold target.

If the electron emission from a hot target is plotted against the velocity rather than the energy of the helium ions, the curve obtained is even more striking, fig. 5. The rate of increase of emission at a velocity of about 2×10^7 cms. per second is extraordinarily sharp.

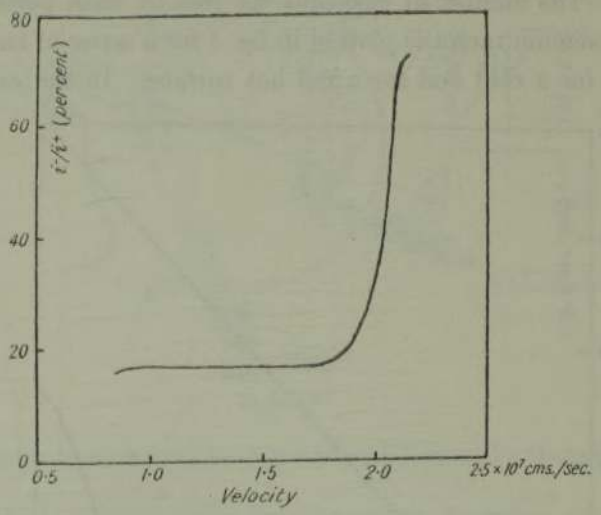

Fig. 5.

(*b*) *The Effect of Variation of the Angle of Incidence of the Bombarding Ions.*—The measurements which we have described were carried out with normal incidence of the ions upon the target. The apparatus is so constructed that the angle of incidence could be varied by rotating the ground joint which carried the target.

The secondary emission was found to increase with the angle of incidence of the ions.* The results of a series of measurements with a nickel target are graphically depicted in fig. 6. A very good straight line is obtained from all the measurements so far made, if the total emission is plotted against the cosine of the angle of incidence, for a hot or for a gas-covered surface. The emission is therefore proportional to $(1 - \cos \theta)$. This law was found to hold for a molybdenum surface polished to a good mirror, or for a nickel surface polished very roughly with fine emery paper. It was not possible to carry the measurements to very glancing angles, owing to the finite width of the beam of ions, which caused some of them to miss the target at angles of incidence greater than about 60°.

* This increase of electron emission with angle of incidence has been observed by Saxen, 'Ann. Physik,' vol. 38, p. 319 (1912), in the case of relatively fast canal rays.

(c) *The Velocity Distribution of the Secondary Electrons.*—The energy distribution of the secondary electrons was determined both by the retarding

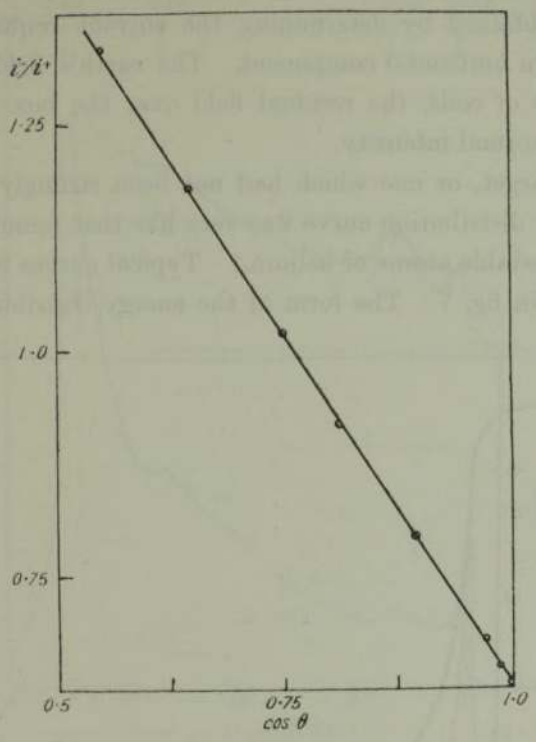

FIG. 6.

potential method and by the magnetic deflection method of analysis. A large number of curves have been obtained under very varying conditions of the target surface, and for a large range of energy of the incident ions. The magnetic method fails for velocities below about 2·8 volts, probably on account of uncompensated magnetic fields, or to contact potential differences due to different gas-conditions of the target and slits. Contact potentials between the target and the collecting sphere in the retarding potential apparatus were eliminated by heating the target to about 1200° C., at which temperature the thermionic electron emission from the large area could be detected on a sensitive galvanometer, and determining the potential difference which would just prevent emission. The correction for contact potential was usually of the order of 0·4 volt, the collecting sphere being negative with respect to the target. The same correction was determined experimentally for a cold target by illuminating strongly with light from an arc and using the photoelectric characteristic, or by observation of the known velocity distribution of the

electrons liberated by the impact of metastable atoms of helium formed in the canal of the discharge tube.* The magnetic apparatus was calibrated absolutely by calculation from the dimensions of the box and the Helmholtz coils, a check being obtained by determining the current required to neutralise the earth's known horizontal component. The earth's field was neutralised by suitable pairs of coils, the residual field over the box being less than $\frac{1}{2}$ per cent. of the normal intensity.

With a cold target, or one which had not been strongly heated for some time, the velocity distribution curve was very like that found for the electrons liberated by metastable atoms of helium.† Typical curves for a molybdenum target are given in fig. 7. The form of the energy distribution appeared to

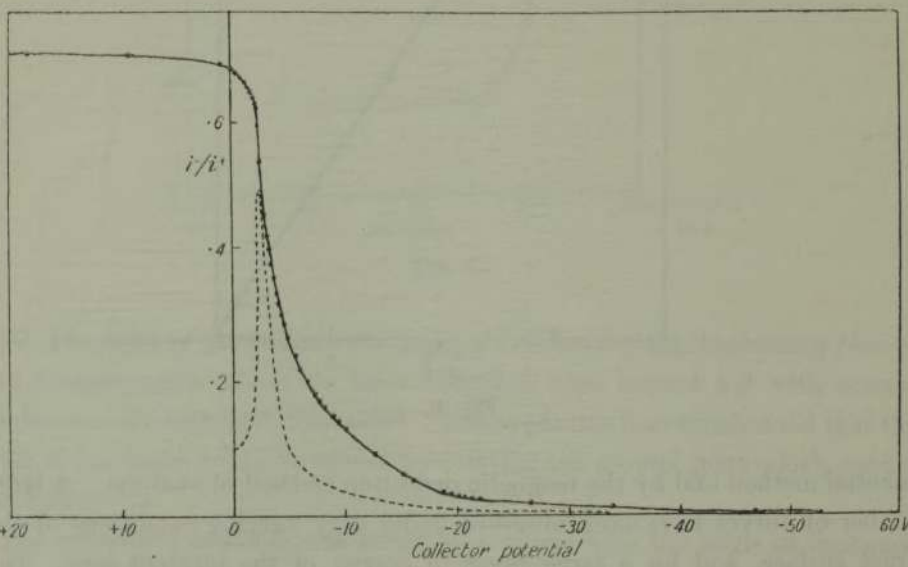

Fig. 7.—Retarding Potential Curve for the Electrons set free from a gas-covered surface of Mo by He^+ ions of 400 volts energy. The dotted curve is the velocity distribution derived from it.

be practically independent of the velocity of the impacting ions in the range from 120 to 1000 volts.

After long continued heat treatment of the target, and purification of the helium, the velocity distribution curve changed its character. The total number of electrons ejected was smaller than for a gas-covered surface, but the relative number possessing the higher energies increased considerably (fig. 8). The curve was no longer smooth, but exhibited a number of maxima.

* *Loc. cit.*, p. 13, footnote.

† *Loc. cit.*

the most prominent, and most consistent in occurrence, being at 2·5, 6·8, 17·0 and 20 volts. There was a very sharp cut-off at approximately 20·2

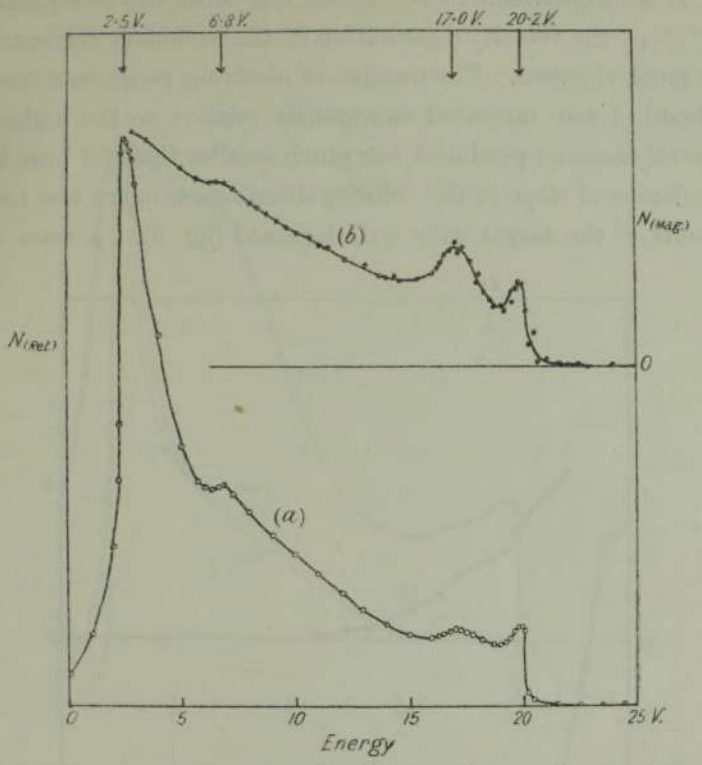

FIG. 8.—Velocity Distribution Curve for this Electrons liberated from gas-free Mo by He^+ ions of 400 volts energy. (*a*) Retarding Potential Method. (*b*) Magnetic Analysis.

volts, while the retarding potential curve revealed a low velocity cut-off, almost as pronounced, at 2·3 volts. The position of these maxima, as well as of the upper and lower limits, did not differ by more than a fraction of a volt for the three materials for which they have been obtained, Ni, Mo and W. There is some evidence of their presence with a platinum target, but Al, Cu and Ag gave a smooth curve of the type obtained with gas-covered Ni or Mo. These materials are very difficult to outgas thoroughly without melting them. Molybdenum, however, gave by far the most consistent results of any material tested, and the results obtained for this metal are given in the graphs in this paper.

It was not possible to retain liquid air on the trap between the diffusion pump and the apparatus overnight, so that when starting a run in the mornings a certain amount of mercury vapour was always found to have diffused over into the discharge chamber O, fig. 1. This was soon swept away if the apparatus

was heated to about 200° C. and the helium allowed to circulate for 15 minutes or so, and its removal could be followed by observation of the spectrum from the arc. If an experiment was carried out with the composite beam of $He^+ + Hg^+ + \ldots$ the velocity distribution of the secondary electrons was found to be very much changed. The number of electrons possessing energies in the neighbourhood of zero increased enormously relative to the higher velocities, while the total emission produced was much smaller than for pure helium ions. A distinct change of slope in the velocity distribution curve was found at very nearly 6 volts, if the target were well degassed (fig. 9). A trace of impurity

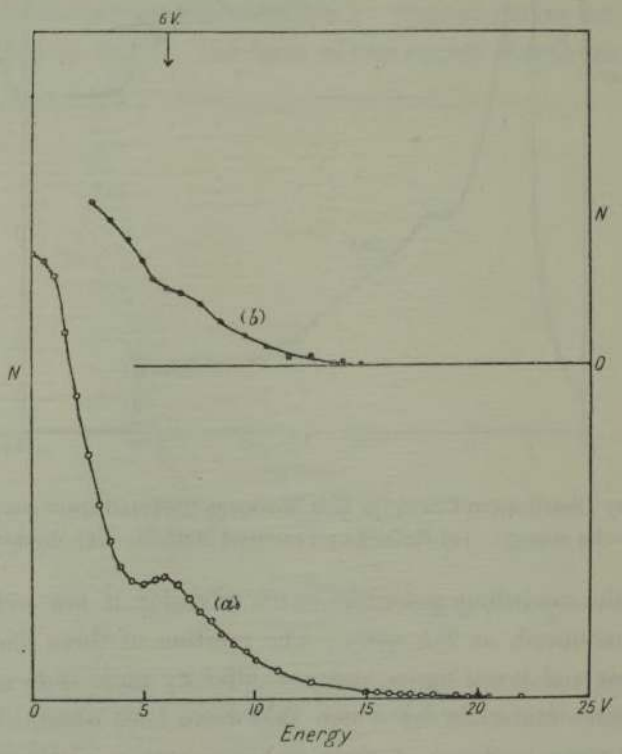

FIG. 9.—Energy Distribution for the Electrons set free from hot Mo by $He^+ + Hg^+ + Hg^{++} + \ldots$. (*a*) Retarding Potential Method. (*b*) Magnetic Analysis.

which could only just be detected spectroscopically, completely destroyed the clear-cut character of the distribution curve produced by He^+ ions. Indeed, it was only after purification had been carried out for several hours after the spectroscopic disappearance of impurities that the curve assumed its final form as shown in fig. 8.

The intensity of the 20-volt maximum increased with the velocity of the ions. With an accelerating potential of 200 volts it was just noticeable, while

at 400 volts it was very pronounced and exceedingly sharp, fig. 10. At potentials greater than about 700 volts the maximum began to spread, mainly

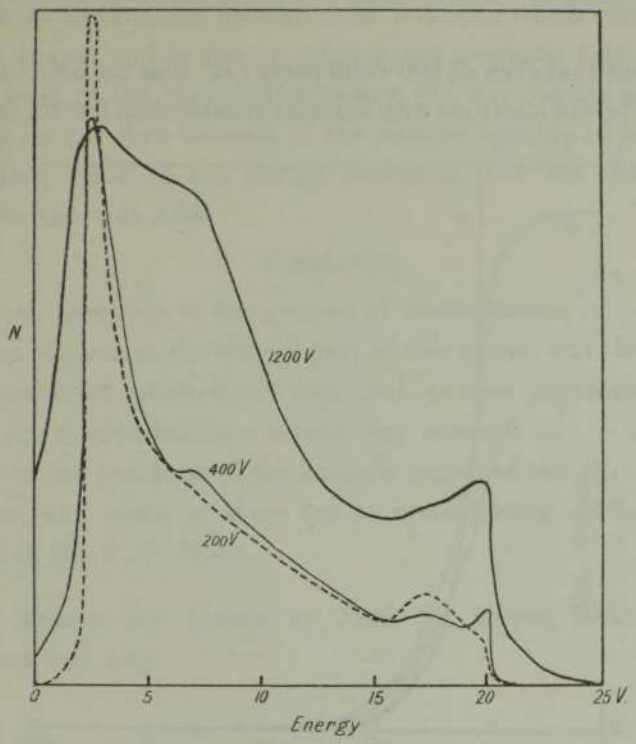

FIG. 10.—Energy Distribution of the Electrons liberated from degassed Mo by He^+ ions of various energies (Retarding Potential Method).

towards the low velocity side, till at 1200 volts the curve had assumed the shape plotted in the graph. The lower energy portion of the distribution curve did not undergo any radical change with the energy of the bombarding ions below 1500 volts, but above this it began to spread, becoming very diffuse at 5000 volts.

Experiments with Alkali Ions.

It is shown in the second portion of this paper that the emission of secondary electrons is profoundly influenced by the relative values of the ionisation potential of the atom from which the bombarding ion originated, and the work function of the struck surface. The cases which we have so far considered were such that the ionising energy was far greater than the work function of the surfaces, and it is desirable to have results obtained when this position is reversed. For this reason some experimental curves are given which show the velocity distribution among the electrons ejected from various surfaces

by singly charged potassium ions from a thermionic source. The apparatus used has already been described,* and the retarding potential curves given in fig. 2 were obtained at the same time as the experimental results given in that paper.

It is apparent that even at 600 volts energy K^+ ions are able to set free considerable numbers of electrons with energies greater than 5 volts, from platinum

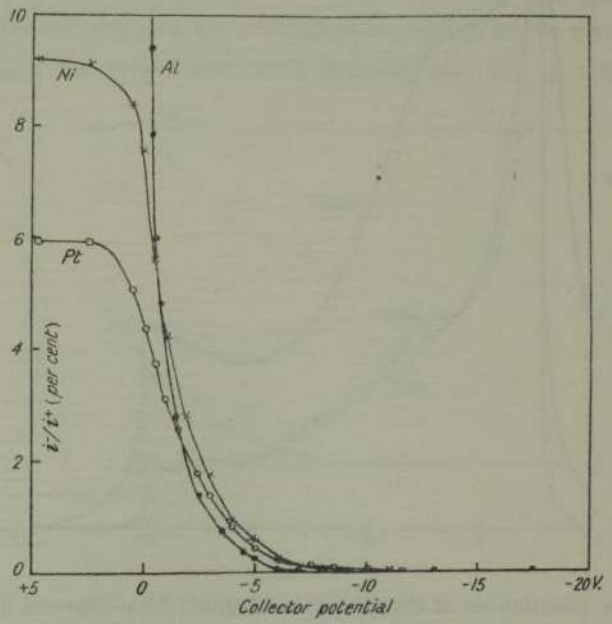

Fig. 11.—Retarding Potential Curves for the Electrons set free from various metals by K^+ ions of 600 volts energy.

or nickel surfaces. There appears to be a greater relative number of low velocity electrons from an aluminium surface than from nickel or platinum, whose work functions are considerably higher. An untreated surface of any metal, freshly introduced into the apparatus, always gives a much greater emission than a cleaner one, but the relative number of the high velocity electrons is small. Surface factors which increase the magnitude of the emission always tend to decrease the relative number of the electrons with higher energies. This is also true of the electron emission produced by He^+.

The maximum of the velocity distribution curve, for the electrons liberated by the impact of low velocity alkali ions, always occurs in the neighbourhood of zero energy. There is a greater probability that an electron will possess just sufficient energy to escape from the surface than that it should escape with

* Oliphant, 'Proc. Camb. Phil. Soc.,' vol. 24, p. 451 (1928).

any considerable velocity. (The fact that a collecting potential of a volt or so is required in order to collect the total emission on the bulb is probably due to the contact differences of potential which exist between the bulb and the target, and to the uncompensated magnetic field of the earth.) The general form of the energy distribution did not change much with the energy of the ions, a slow increase in the relative number of higher velocity electrons taking place as the energy increased, but the curves remained exponential to the volt axis.

Conclusion.

A theoretical discussion of the process of neutralisation of positive ions at metal surfaces is given in the second part of this paper, and the experimental results here presented satisfactorily explained, at least qualitatively. Further experiments are needed before a satisfactory attempt can be made to apply these results to the problems of the cathode region of the electrical discharge through gases, and some of these are at present being carried out with the collaboration of Mr. P. B. Moon.

I wish to express my thanks to Prof. Sir Ernest Rutherford for his encouragement and help.