Electron Temperatures in Electrical Discharges

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Electron temperatures in the positive column and in the Faraday dark space of a cold cathode glow discharge have been measured by the probe method when the gas pressures of dry air and carbon monoxide were varied in the range from 0.06 to 1.2 mm Hg. For the fast group, electron temperatures decrease with pressure while for the slow group they are independent of it. The electron current densities increase and the space potentials decrease when the gas pressure is increased. Different current-voltage characteristic curves have been found in the positive column and in the transition region from the negative glow to the Faraday dark space. Theoretical interpretations of these different characteristics could be obtained either from Langmuir's theory of probe or from Druyvesteyn's theory of electron energy distribution by assuming the existence in the boundary between negative glow and Faraday dark space of a drift fast electron beam superimposed upon an isotropic slow electron distribution. Spectroscopic investigations of the bands of the neutral and ionic molecules of N_2 and CO in different sections of discharges also support the supposition.

1. INTRODUCTION

OUR knowledge of the mechanism of the glow discharge has not been advanced greatly, partly because the fundamental processes are only in a small part quantitatively known, and partly because of mathematical difficulties[1–4] which arise in the description of the observed phenomena of the discharge. But it has been established that, in order to maintain a self-sustained electrical discharge, the electrons generated in the cathode region are mainly due to the γ-process, which gives electron liberation at the cathode by positive ion impact.[5–8] These electrons are accelerated in the cathode fall space and move with nearly a homogeneous velocity towards the anode.[9] Of course, most of the primary electrons are scattered in their paths and retarded by collisions with gas molecules. The light emission in the negative glow is probably due to the result of the excitation of the gas molecules by these fast electrons entering this section of discharge from the Crookes dark space.

Probe measurements[10–11] indicate that fast electrons with energies of the order of that obtained by passing through the cathode fall space are present in the Faraday dark space and sometimes in the positive column and that they are distributed according to the Maxwell-Boltzmann law. Some authors,[10,12] however, suspect that the primary electrons from the cathode dark space are able to penetrate far into the negative glow or even into the Faraday dark space, and it was suggested that these electrons are formed by some mechanism of the converse of ionization by collision, when a system of two slow electrons and one positive ion pass into a unit consisting of an excited molecule and a single fast electron. In a neon glow discharge Druyvesteyn[13] has observed spark lines with high excitation energies, which proves that electrons exist with an energy corresponding to more than 80 percent of the cathode fall. But the concentration of these electrons could not be determined. A direct determination of the energy of the electrons[14–15] showed that for a cathode fall above 400 volts, most electrons in

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[2] J. J. Thomson, Phil. Mag. **8**, 393 (1929).
[3] W. Rogowski, Archiv. f. Elektrotechnik **26**, 643 (1932).
[4] W. Weizel, R. Rompe, and M. Schon, Zeits. f. Physik **112**, 339 (1939); **113**, 87 and 730 (1939).
[5] H. A. Wilson, Phys. Rev. **8**, 227 (1916).
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[9] J. J. Thomson, Phil. Mag. **48**, 4 (1924).
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[11] K. G. Emeleus, W. L. Brown, and H. M. Cowan, Phil. Mag. **17**, 146 (1934).
[12] K. G. Emeleus and O. S. Duffendack, Phys. Rev. **47**, 460 (1934).
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[14] A. K. Brewer and J. W. Westhaver, J. App. Phys. **8**, 779 (1937).
[15] J. F. Lehmann, Proc. Roy. Soc. **A115**, 624 (1927).

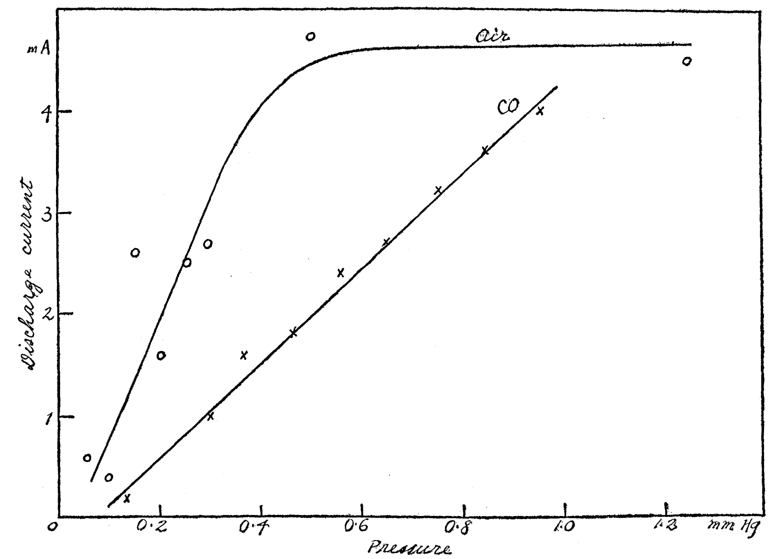

FIG. 1. Variation of tube current with gas pressure.

the negative glow had an energy which was almost equal to the cathode fall. Determinations of this kind, however, are not very reliable as a third electrode which disturbs the discharge must be brought into the negative glow. In the present investigation it is attempted to show the existence, in the transition region from negative glow to the Faraday dark space, of primary electrons coming from the cathode dark space. Probe measurements have been made in the positive column and in the Faraday dark space when the gas pressures in the discharges were varied. Different current-voltage characteristic curves in these two regions have been found. Theoretical interpretations of these different characteristics could be obtained either from Langmuir's theory[16–17] of probe or from Druyvesteyn's theory[18] of electron energy distribution by assuming the existence in the boundary between negative glow and Faraday dark space of a drift fast electron stream superimposed upon an isotropic slow electron distribution. Spectroscopic investigations of the bands of the neutral and the ionic molecules of N_2 and CO in different sections of discharges also support the supposition.

[16] I. Langmuir, Phys. Rev. **26**, 585 (1925).
[17] H. M. Mott-Smith and I. Langmuir, Phys. Rev. **28**, 727 (1926).
[18] M. J. Druyvesteyn, Zeits. f. Physik **64**, 781 (1930); Physica **10**, 69 (1930).

2. APPARATUS

The form of the discharge tube used was cylindrical, 2 cm in diameter and 10 cm in length with two aluminum disk electrodes of 1.2 cm diameter sealed through a CR lead-in wire coaxially on each end of the tube at a separation of about 7 cm. The probe was a 6-mil tungsten wire 6 mm long and spot-welded to a lead-in wire mounted in a small glass tube fused perpendicularly to the discharge tube at a distance of about 1.5 cm from one of the disk electrodes. The discharge tube was sealed by means of a side-tube on to the vacuum system made of soft glass tubings, and pumped by a Cenco steel mercury diffusion pump backed by an oil pump. The pressures in the tube were measured by two McLeod gauges for different ranges. The discharge tube and electrodes were degassed by running a discharge with an induction coil and pumping out alternatively over days.

The gases used were dry air and carbon monoxide. The latter was generated by heating oxalic acid in the presence of concentrated sulfuric acid, carbon dioxide gas and water vapor being removed by lime water and anhydrous phosphorus pentoxide, respectively. Before being employed to take readings the vacuum system and tube were flushed a few times with the gases. Because the gas pressure was not too low and the discharge temperature was not more than 35°C, it

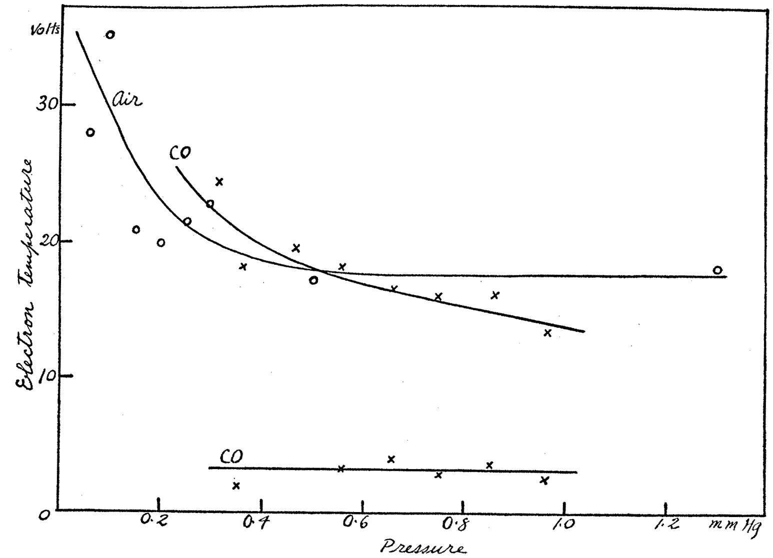

FIG. 2. Variation of electron temperature with pressure. Upper curves, fast group; bottom curves, slow group.

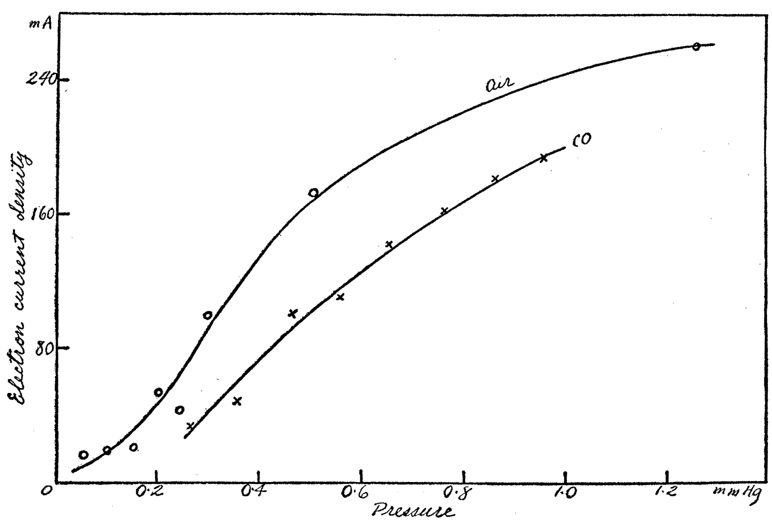

FIG. 3. Variation of electron current density with pressure.

was thought not worth while to use liquid air to remove any residual mercury vapor in the tube although traps were provided on the vacuum system.

The discharge was excited by a 500-volt rectifier stabilized by neon bulbs, with one of the electrodes grounded. The wiring in the probe circuit was arranged in the usual way. The potential of the probe was varied and the current-voltage characteristic values were obtained by means of a microammeter in combination with a universal shunt so that the current could be measured conveniently from a few microamperes to a few milliamperes.

3. EXPERIMENTAL RESULTS

In the gas pressure range between 0.06 and 1.2 mm Hg with a potential of 500 volts applied across the discharge tube, the tube current was a few milliamperes and so the discharge was probably of the normal glow type. On the anode side two or three striations could usually be observed. They were particularly sharp in the case of carbon monoxide gas. As the gas pressure was increased in the above-mentioned range, the discharge current increased linearly in the case of CO, but for air after 0.5 mm Hg the current seemed to approach a constant value as shown in Fig. 1.

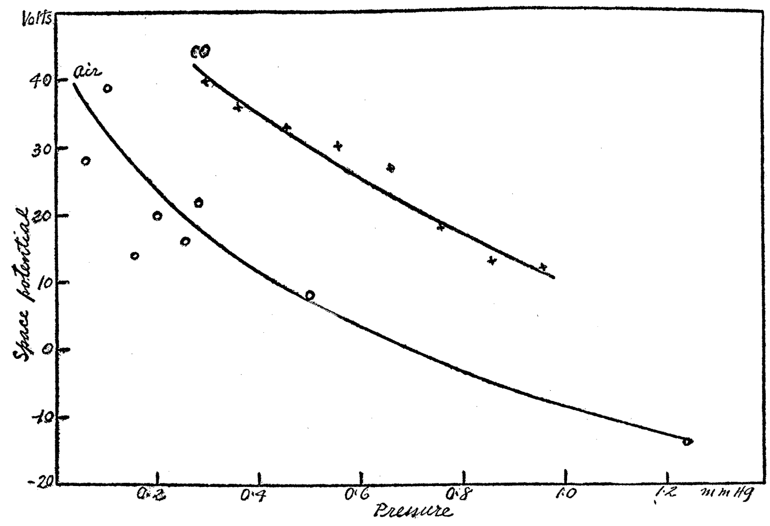

FIG. 4. Variation of space potential with pressure.

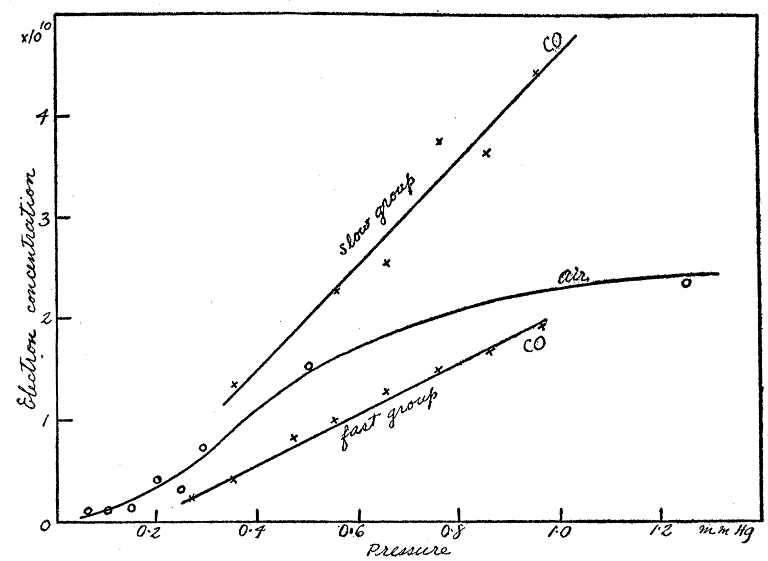

FIG. 5. Variation of electron concentration with pressure.

When the probe was at a very negative potential with respect to the anode, only a positive ion current was recorded. By decreasing the retarding potential the positive ion current at first diminished linearly and then rather rapidly, because some electrons of higher velocities were able to penetrate through the ion sheath around the probe and then were collected by the latter. As the retarding field was made still weaker, electrons of lower velocities could also be collected by the probe. Then an electron current became appreciable and continuously increased until one came to a point where the potential of the probe was the same as that of the surrounding ionized gas. In analyzing the characteristic data, a large scale plot of positive ion current *versus* probe potential was made. The extrapolation of the straight line tangent to the ion current to the smaller negative voltages gave the contribution of the positive ions to the current, and the electron current could then be obtained from the difference between this and the total observed current at that potential. In the regions of the positive column and the Faraday dark space near the anode side in the discharge, typical semi-logarithmic plots of electron current against retarding potentials are similar to the *B* curves in Figs. 6 and 7.

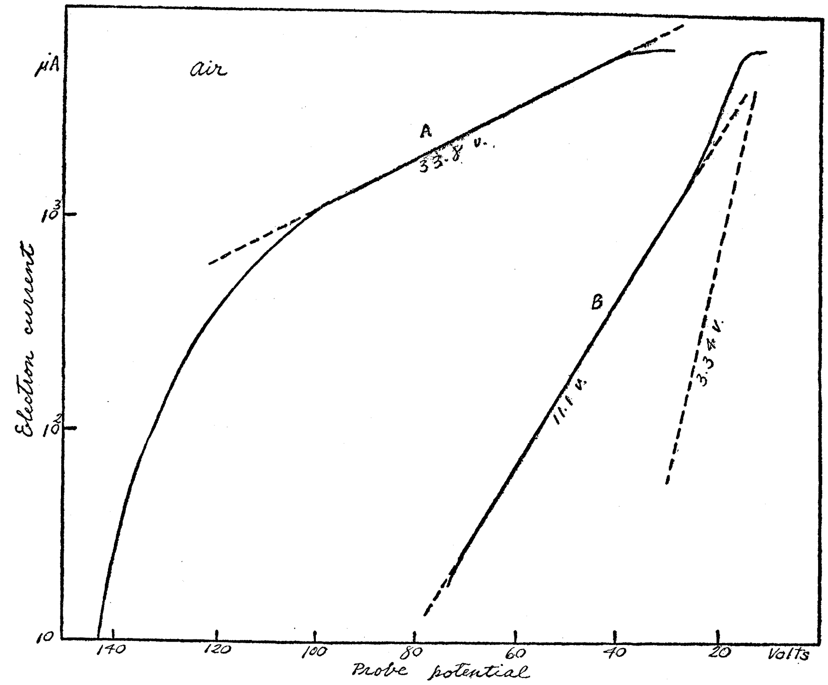

FIG. 6. Current-voltage characteristics in air discharge at a gas pressure 1.25 mm Hg, tube voltage 490 volts, tube current 4.5 ma. Curve A in Faraday dark space, curve B in positive column.

If the velocities of the electrons were described by a Maxwell-Boltzmann distribution, the semi-logarithmic plot would be, according to the probe theory of Langmuir and Mott-Smith,[19] a straight line, of which the slope determined a temperature corresponding to the electron velocities. At higher retarding potentials the observed deviation from linearity indicates that the distribution of electron velocities in the discharge must be rather complicated. However, one might assume that there existed more than one group of electrons, each of which was distributed according to Maxwell's law. The slope of the straight line drawn along the higher retarding potential characteristic curve gave the temperature of the fast electron group, and the slope of another straight line determined from the differences between the extrapolation of the first straight line and the observed values gave the temperature of the slow electron group. Sometimes a third electron group was observed. In the case of a discharge in CO, the second group came out quite definitely and was analyzed. In the case of air, the presence of the second group was revealed only at higher pressures.

[19] I. Langmuir and H. M. Mott-Smith, Gen. Elec. Rev. **27**, 449, 538, 616, 762, and 810 (1924).

Figure 2 gives the data obtained for the variation of the electron temperature with pressure. For the fast group, electron temperatures decrease strongly when the pressure was increased, while for the slow group, the electron temperature is independent of the pressure.

Figure 3 shows the data for the variation of the electron current density with pressure.

Figure 4 presents data for the change of space potentials at a point in the discharge when the pressure was increased.

Electron concentrations in the ionized gas can be calculated from the relation

$$n=(I/e)(2\pi m/kT)^{\frac{1}{2}},$$

where e and m are the charge and mass of the electron respectively, k is the Boltzmann constant, I is the electron current density, and T is the electron temperature. The results of the calculation are plotted in Fig. 5.

Figures 6 and 7 are the current-voltage characteristic curves in air and CO respectively for discharges in the Faraday dark space near the boundary with the negative glow (curves A) and in the positive column (curves B). These two regions yielded quite different characteristic curves. Near the space potential on the characteristics we had a straight line portion in the Faraday dark space, which determined a temperature if the part of the characteristic at the higher retarding potentials was neglected. In the case of air at a pressure of 1.25 mm Hg this determined temperature is higher than the temperature of the fast group in the positive column, while in CO at a pressure of 0.87 mm Hg the determined temperature is lower than that in the positive column.

4. INTERPRETATION OF THE VARIATION OF ELECTRON TEMPERATURES AND SPACE POTENTIALS WITH PRESSURE

The observation of the decrease of electron temperature with pressure is quite similar to the measurements of Seelinger and Hirchert[20] in the positive column of neon and argon discharges, of Groos[21] in argon, and of Klarfeld[22] in mercury. As the pressure increases, there are more chances for the electrons to impact with gas molecules and consequently the mean kinetic energy of electrons will be diminished because of energy loss. Hence the electron temperature decreases. The slow electrons are formed from primaries after being scattered and retarded by numerous collisions with gaseous molecules. Since these ultimate electrons have already suffered many elastic impacts, further change of pressure will not probably influence their mean kinetic energy. Thus the slow electron temperature keeps constant with pressure variation.

By comparing the values given in Fig. 2 with that in Fig. 4 for any given gas pressure, one finds that the electron temperatures decrease with space potential, because in weaker fields electrons gain lower energy. This is in agreement with the observations of Duffendack and Chao[23] who found that electron temperature diminishes as one goes from cathode to anode in a nitrogen glow discharge.

5. TRANSLATIONAL AND RANDOM ELECTRON VELOCITIES

The difference of the volt-ampere characteristic curves obtained at the junction of the Faraday dark space with the negative glow and in the positive column does not seem to be explained by merely dividing electrons into isotropic Maxwellian groups, because it is not reasonable to neglect the electron current for higher retarding potentials in the characteristic curve from the dark space. These characteristics, which are concave downwards for a considerable part in higher retarding potentials, are different from the anomalous curves discussed by Emeleus and Brown,[24] and must be due to some causes other than positive space charges.

Let us assume that the resultant velocity distribution of the electrons near the Faraday dark space can be analyzed into a part with uniform translational motion and a superposed Maxwellian part with temperature motion, and that the velocities due to isotropic temperature motion are small compared to those of transla-

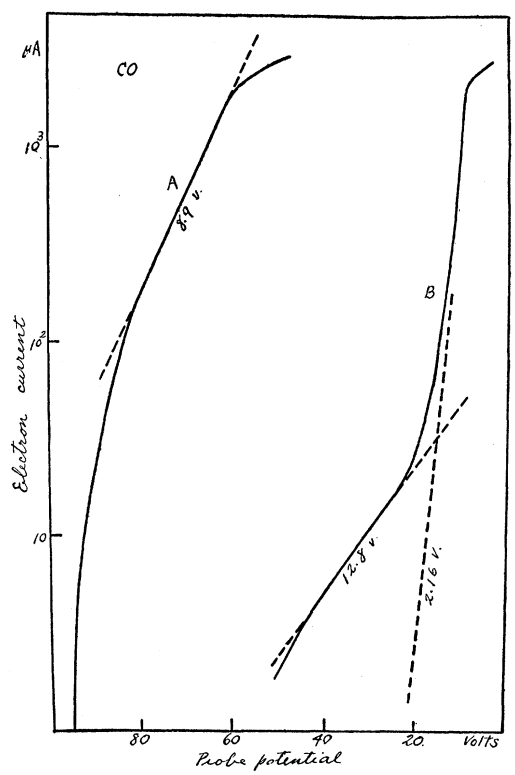

FIG. 7. Current voltage characteristics in CO discharge at a gas pressure 0.87 mm Hg, tube voltage 520 volts, tube current 3.4 ma. Curve A in Faraday dark space, curve B in positive column.

[20] R. Seelinger and R. Hirchert, Ann. d. Physik **11**, 817 (1931).

[21] O. Groos, Zeits. f. Physik **88**, 741 (1934).

[22] B. Klarfeld, Tech. Phys. USSR **4**, 44 (1937); **5**, 725 and 919 (1938).

[23] O. S. Duffendack and K. T. Chao, Phys. Rev. **56**, 176 (1939).

[24] K. G. Emeleus and W. L. Brown, Phil. Mag. **22**, 898 (1936).

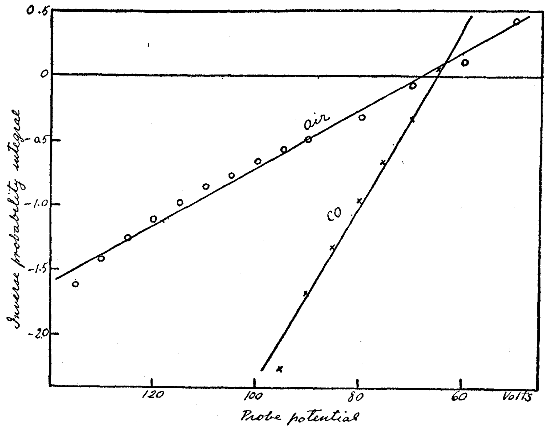

FIG. 8. Inverse probability integral against probe potential.

tion. The theory of the current to a cylindrical probe with its axis perpendicular to the direction of a stream of the drift electrons superimposed on a Maxwellian distribution has been treated by Mott-Smith and Langmuir,[17] and the result is expressed in a quite complicated series. However, in the region where the retarding potential of the probe is less than the equivalent voltage of the drift electrons, the volt-ampere characteristic of a cylindrical probe is nearly the same as that of a plane probe placed perpendicularly to the direction of the drift velocities. Langmuir[16,25] has shown that if I_0 is the current when all the electrons are collected by the probe, the electron current on the probe is given by

$$I=(I_0/2)[1+P(-\lambda)], \quad (1)$$

where $P(-\lambda)$ stands for the probability integral

$$P(-\lambda)=(2/\sqrt{\pi})\int_0^{-\lambda} \exp(-x^2)dx. \quad (2)$$

Here λ is proportional to the difference of the velocity of the electron in the mass-motion and the velocity component of any considered electron in the same direction, or defined by the relation

$$\lambda=(\sqrt{V_t}-\sqrt{V_p})/\sqrt{V_M}. \quad (3)$$

Here V_p is the retarding potential of the probe with respect to the ionized gas (or the sum of the potential of the probe with respect to the ionized gas and of the space potential), V_t is the potential corresponding to the drift velocity of the primary electrons, and V_M is the potential corresponding to the temperature motion. If V_t and V_p are not too far from each other, the geometrical mean $(V_tV_p)^{\frac{1}{2}}$ can be replaced by the arithmetical mean $\frac{1}{2}(V_t+V_p)$. Equation (3) becomes

$$\lambda=(V_t/V_M)^{\frac{1}{2}}-\left[\frac{(V_t+V_p)}{(2(V_tV_M)^{\frac{1}{2}})}\right].$$

Thus λ is a linear function of the probe potential. From Eq. (1) and Eq. (2) we have

$$P^{-1}((2I-I_0)/I_0)=\text{constant}+V_p/2(V_tV_M)^{\frac{1}{2}}. \quad (4)$$

If the plot of the inverse probability integral against the probe potential is a straight line, the supposition of the existence of the superposition of the drift electrons upon a Maxwellian group is confirmed. The intersection of the straight line with the zero line determines the average energy of the drift electrons and the slope gives that of the random electrons. Figure 8 is such a plot from Eq. (4), and the results show that the observed values fall fairly well on straight lines and thus the experiments justify our separation of the electrons into translational and random parts.

In the case of air the straight line intersects the zero line at 68 volts.[26] This is the average energy of the electron beam, while the value directly determined from the curve A in Fig. 6 is only 50.7 volts, since in the latter method of determination the higher energy electrons have been neglected. From the slope of the straight line we have

$$2(V_tV_M)^{\frac{1}{2}}=44.8. \quad (5)$$

The cathode fall potential was not measured, and the fastest electrons that were collected by the probe have an energy about 102 volts, which could not be accurately determined. If this value is taken as the energy of the electron beam, from Eq. (5) we have $V_M=4.93$ volts, which determines the temperature assigned to the random electrons. In the positive column the slow electrons have a temperature corresponding to 3.34 volts. Thus these two methods give about the same value of temperature for the slow electrons.

In the case of CO, the determined average

[25] I. Langmuir, Zeits. f. Physik 46, 271 (1928).

[26] The value thus determined may not be very accurate because of use of the theory of current-voltage characteristics for a plane collector.

energy of the drift electrons is 65 volts and the directly measured value from curve A in Fig. 7 is only 13.4 volts. The energy of the fastest electrons that reach the probe is 35 volts, while the average energy is 65 volts, so the primary electrons can not have energies less than this. If $V_t=65$ volts and $2(V_tV_p)^{\frac{1}{2}}=15.2$, one finds $V_M=0.89$ volt. In the positive column the slow electrons have a temperature of 2.16 volts, which is a little higher.

6. ENERGY DISTRIBUTION OF ELECTRONS IN POSITIVE COLUMN AND IN FARADAY DARK SPACE

If it is assumed that an electron with a given velocity has angles of incidence upon the surface of the sheath of the probe less than a limiting value determined by the retarding potential, the energy distribution of the electrons can be derived. Druyvesteyn[18] has obtained a distribution function in the form

$$\rho\left[\frac{2e(V_g-V_p)}{m}\right]^{\frac{1}{2}}=\frac{4m}{e^2A}(V_g-V_p)\frac{d^2i}{dV_p^2},$$

where e and m are the charge and mass of the electron, A the surface area of the probe, i the electron current, and V_g and V_p are the gas and probe potentials respectively. Hence the measurement of the curvature of the current-voltage

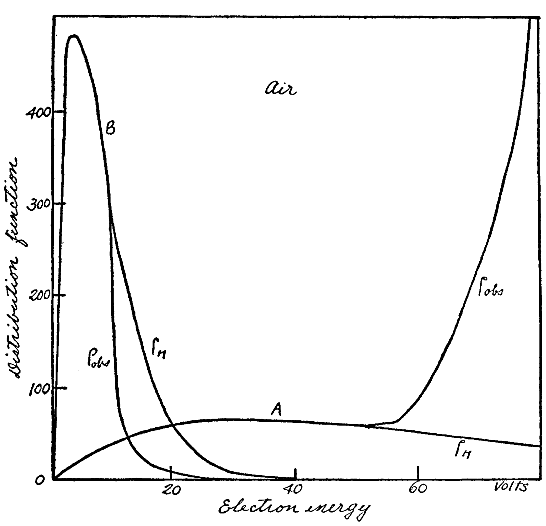

FIG. 9. Observed electron energy distributions compared with Maxwellian distributions. Curve A for Faraday dark space, curve B for positive column.

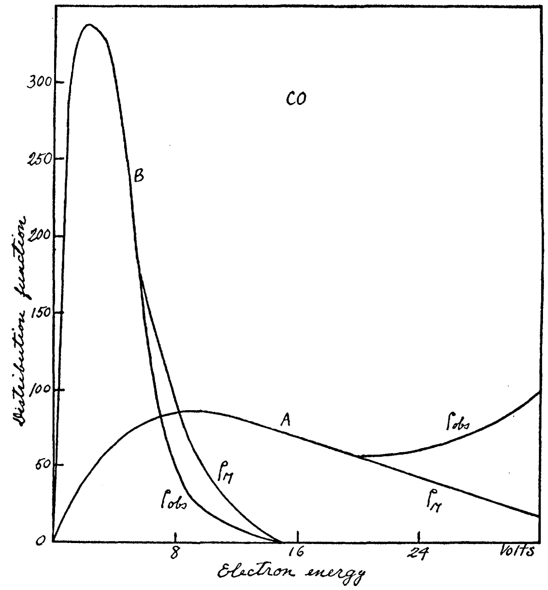

FIG. 10. Observed electron energy distributions compared with Maxwellian distributions. Curve A for Faraday dark space, Curve B for positive column.

characteristics will yield the distribution function. The double differentiation from the characteristic curve, however, presents difficulties due to inevitable slight experimental errors. To simplify the operation of the double differentiation, Sloane and Emeleus,[27] by making use of a mathematical identity, have obtained a modified formula

$$\rho\left[\frac{2e(V_g-V_p)}{m}\right]^{\frac{1}{2}}=\frac{4m_i}{e^2A}(V_g-V_p)\left[\left(\frac{d\log i}{dV_p}\right)^2+\frac{d^2\log i}{dV_p^2}\right]. \quad (6)$$

In a semi-logarithmic plot the current-voltage characteristic is straightened and the determination of the second derivative is much facilitated. In the case where the semi-logarithmic plot has a linear portion, the second derivative of $\log i$ with respect to V_p vanishes, while the first derivative is a constant.

Curves B and A in Figs. 9 and 10 are the distribution functions of electrons calculated from Eq. (6) in the positive column and in the Faraday dark space respectively. In the positive column of

[27] R. H. Sloane and K. G. Emeleus, Phys. Rev. **44**, 333 (1933).

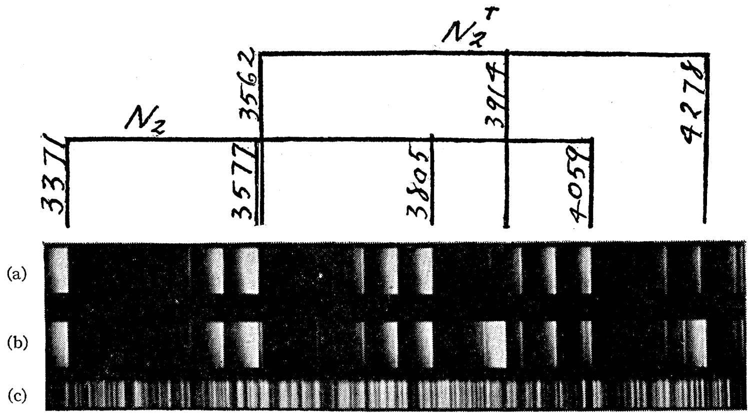

FIG. 11. Spectrogram in air discharge. (a) in positive column, (b) in negative glow, (c) Fe arc.

air discharge, the number of electrons observed with energy greater than 10 volts is less than that calculated from a Maxwellian distribution. Similarly in the CO discharge, for energies greater than 6 volts, the observed and calculated distribution functions begin to diverge. These observations are similar to those of Druyvesteyn,[18] and of Sloane and Emeleus[27] in the positive column of low voltage arcs in neon and argon. The observed number of electrons with about 14 volts in air or with about 11 volts in CO is particularly smaller probably because the energies of those electrons have been used up to excite the N_2 or CO molecules, whose observed excitation potentials[28] have values mostly less than those voltages.

In the Faraday dark space the distribution functions have a quite different form. For higher energies the number of electrons observed is so large that the Maxwellian distribution is negligible. These large values correspond to the points in the semi-logarithmic plot, where the portion of the curve has a curvature concave to the axis of voltage. The results of the distribution plot again show that in this section of discharge a fast electron stream is superimposed upon a small random electron distribution. The presence of this fast electron stream is of particular interest in the consideration of the excitation of molecular spectra in electrical discharges.

7. ELECTRON ENERGIES AND MOLECULAR SPECTRA

In order to get some information about the collisions of electrons with gas molecules, spectroscopic studies were made on the regions of the negative glow near the Faraday dark space and the positive column in air and CO discharges. An image of the positive column in air was focused by means of a condensing lens on the slit of a Hilger E-1 spectrograph. The second positive bands of N_2 are very intense on the photographs taken with Eastman Kodak plates at an exposure of about 70 minutes. When the negative glow was thrown close to the slit, the first negative bands of N_2^+ are relatively stronger than the positive bands at an exposure of about 40 minutes, both bands being on the same plate in this spectral region as shown in Fig. 11. The excitation potential for bands of the second positive system is 13 volts and the simultaneous ionization and excitation of the first negative system require 19.6 volts.[29] In the positive column the fast

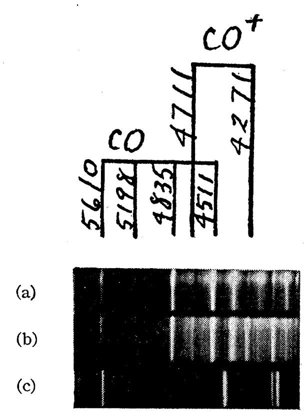

FIG. 12. Spectrogram in CO discharge (a) in positive column, (b) in negative glow, (c) Hg arc.

[28] W. Jevons, *Report on Band Spectra of Diatomic Molecules*, pp. 78–82 (1932).

[29] Recent studies of the excitation of N_2 and N_2^+ bands have been published in two papers by R. Bernard and R. C. Pankhurst, Science Abstracts **43**, 917 (1941). These papers, however, are not available here.

electron group has an average energy of 16.6 volts which is sufficient to excite the positive bands but not the negative ones. The negative bands can be easily excited in the negative glow by the fast electrons whose average energy measured is 68 volts. This seems to explain the different appearence of the spectra in these two regions.

In case of CO a Hilger E-2 spectrograph happened to be employed to take pictures of the emission from the positive column and the negative glow. The spectrograms also show some difference in these two regions as seen in Fig. 12. The Angstrom bands of CO on both spectrograms are strong, but few of the comet-tail bands[30-31] of CO^+ come to appear in the negative glow. Probably some of the Baldet-Johnson bands are also present. The excitation potential of the Angstrom bands is 10.7 volts, while that for the comet-tail bands is 16.7 volts. In the positive column the fast electrons have an energy of 19.2 volts, but in the region of transition from negative glow to Faraday dark space they have 65 volts. It is obvious that the molecular ions are easily excited in the negative glow. That much higher energies are used to excite the bands of the molecular ions than that needed for the simultaneous ionization and excitation, is because of the probability of excitation. Experimental investigations of the electron-impact excitation function of the negative bands of N_2^+ and the comet-tail bands of CO^+ have been reported by many people.[32-34] The conclusion is that the excitation functions for N_2^+ and CO^+ molecules behave in a quite similar manner and both functions have a maximum at a potential about 2.5 times the value of the excitation potential. The fact could be explained that though the excitation potential of CO^+ bands (16.7 volts) is less than that of N_2^+ bands (19.6 volts), about the same amount of the electron energies is required to excite these bands.

The authors wish to thank Mr. C. C. Yang who built a part of the vacuum system and Messrs L. Yang and F. S. Li of the Chemistry Department who helped to produce the carbon monoxide gas.

[30] T. R. Merton and R. C. Johnson, Proc. Roy. Soc. **A103**, 383 (1923).
[31] R. C. Johnson, Proc. Roy. Soc. **A108**, 355 (1925).
[32] A. E. Lindh, Zeits. f. Physik **67**, 67 (1931).
[33] R. Bernard, Comptes rendus **204**, 488 (1937).
[34] F. P. Bundy, Phys. Rev. **52**, 698 (1937).

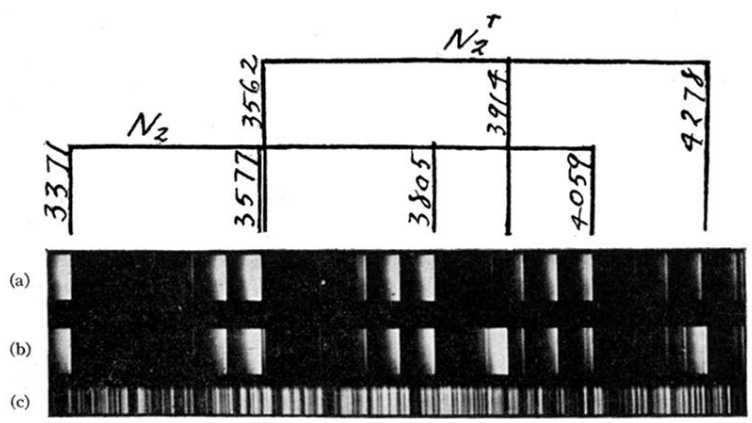

FIG. 11. Spectrogram in air discharge. (a) in positive column, (b) in negative glow, (c) Fe arc.

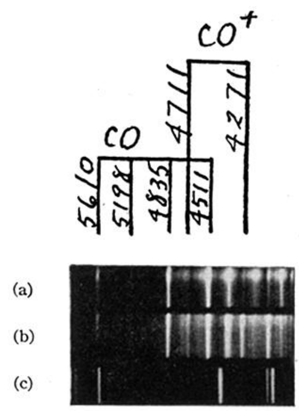

FIG. 12. Spectrogram in CO discharge (a) in positive column, (b) in negative glow, (c) Hg arc.