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The hollow-cathode effect and the theory of glow discharges

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The nature of the processes in the cathode dark space and the negative glow of a glow discharge is not well understood. Moreover, the existing theory leading to relations between the cathode fall in potential, the current density, the width of the dark space and the electric field distribution in it is based on dubious assumptions and does not indicate the important physical processes in operation. Thus further experimental evidence would be valuable in developing the theory.

By exploring the electric field between two plane-parallel cathodes with an electron beam, and observing simultaneously the other discharge parameters, new information was obtained. A double (hollow) cathode was used because in a conventional glow discharge the dark space, cathode fall and current density are interdependent; here the cathode separation controls the width of the dark space. When the separation is sufficiently reduced the two negative glows coalesce and the light emitted as well as the cathode current density rise greatly. This is the hollow-cathode effect.

Results show that the field in the two dark spaces of a hollow cathode falls linearly with the distance from the cathode, and thus the net space-charge density is constant, as it is known to be in the conventional discharge. From the same observations the dark-space length is found.

The conclusions drawn from these results lead to an elementary theory which covers both the hollow and the conventional glow discharge in various gases as indeed it should, since with increasing cathode separation the first goes over into the second type. The main feature is the contribution of the ultra-violet quanta from the glow to the photo-electric emission from the cathodes which is regarded as the essential factor in secondary electron emission. Another result comes from a reconsideration of the motion of positive ions in the dark space based on atomic beam studies and the modern theory of elastic collisions between ions and atoms. The discrepancy between earlier experiments showing that ions of energy of the order of the cathode fall in potential arrive at the cathode and classical calculations leading to low ion energies is resolved by allowing for small-angle scattering and charge transfer.

1. Introduction

The theory of the glow discharge is essentially concerned with the electrical phenomena near the cathode which are closely associated with emission of light and chemical changes in the gas. As to the electrical properties of the glow discharge it is known that in general the larger part of the discharge voltage appears across the dark space adjoining the cathode. For gases free from negative ions this cathode fall in potential is usually several hundred volts, while the negative glow which joins the cathode dark space, and the Faraday dark space beyond the glow require only a small potential drop. The cathode fall and the current density at the cathode remain constant as the current is increased by several orders of magnitude as long as the glow covers only a part of the cathode, but both quantities rise once the glow covers the whole cathode. Very little visible light is emitted from the cathode dark space; owing to the high potential across it the electrons are so fast that they have little chance of exciting molecules to such levels that visible radiation results. This is equivalent to saying that the electrons have energies well beyond the maximum of the corresponding excitation functions. Conversely, when electrons have been multiplied by ionization in the gas and many slow ones have been produced in the region of lower fields, intense excitation and recombination of ions and electrons will occur. In this part of the discharge their space charges become equal and the negative glow appears.

In the development of the theory of the cathode-fall region several phases can be distinguished: in the first the cathode fall was associated with a discontinuous change in potential at the cathode (see Bär 1927); in the second it was treated as a region where positive ions fall freely from the boundary between glow and dark space to the cathode (Ryde 1923). This treatment was improved by assigning a mobility to the charges moving in the dark space (Aston 1923; Thomson 1924). Later the ionization in the gas and the secondary emission from the cathode were introduced and expressed in terms of the corresponding coefficients of Townsend (von Engel & Steenbeck 1934). In all this work the dark space was regarded as an isolated unit. However, in the last phase other cathode regions were included in the theory (Lunt, von Engel & Meek 1941), but the complexity of the analysis made a detailed comparison between these theories and experiments impracticable.

Surprisingly the theory of the dark space in isolation based on the distribution of the electric field as found by Aston (1911) gave results in reasonable agreement with observation. Yet, it was early recognized (von Engel & Steenbeck 1934, p. 69) that the use of ionization coefficients derived from measurements in uniform fields is not strictly permissible because the field in the dark space falls rapidly with increasing distance from the cathode. This, however, leads to an inconsistency: the ionization in the assumed field leads to a distribution of space charge which deviates from the uniform one. This is also borne out by recent measurements (Morton 1946; Johnson 1948) which show that the ionization by electrons in non-uniform fields is quite distinct from that produced by electrons in equilibrium with the field.

Up to the present, theory has been compared with measurements of the electric field, the current density j at the cathode for a given gas density and the applied potential V which was taken to be roughly equal to the cathode fall V_c. In addition, the variation of the length of the dark space, d, was observed visually. It must be borne in mind that V_c, j and d are interdependent in the conventional glow discharge.

There is, however, another form of glow discharge which makes it possible to keep one of these three quantities constant and to find experimentally the relation between the other two. This is the hollow-cathode discharge in which the cathode is a hollow cylinder, spherical segment or simply a pair of plane-parallel plates. It is known that when two plane cathodes are gradually brought together so that their negative glows coalesce, then the cathode current density is found to rise, often by several orders of magnitude at constant discharge potential. This effect occurs in rare and molecular gases (Paschen 1916; Schüler 1926; van Voorhis & Shenstone 1941; Güntherschulze 1924; Lompe 1938; Lompe, Seeliger & Wolter 1939). Simultaneously, the intensity of light emitted by the common glow is greatly increased which makes it an excellent spectroscopic source of visible and ultra-violet radiation containing many spark lines. Moreover, the low cathode-fall energy causes a lower gas temperature than usual, and so line broadening by the Doppler effect is small. The excitation of gases by electron collision has been surveyed by de Groot & Penning (1933).

Of particular interest here is the part played by the vacuum ultra-violet radiation in the discharge. Its existence had been surmised already in early work (Dauvillier 1926; Thomson 1924, 1926; Seeliger 1934). This radiation may eject electrons from the cathode. Early theory accounted for it by using a secondary emission coefficient which included, besides emission by ions and metastable atoms, the photo-electric effect; but its numerical value for cathodes surrounded by a gas and its variations with discharge conditions were not even approximately known. Such is briefly the present state of knowledge in this field.

It is the aim of this paper first to investigate experimentally the hollow-cathode discharge, and to establish a link with the conventional glow discharge, then to give a simple treatment which embraces any glow discharge with plane cathodes and finally to deduce from the available evidence the elementary processes which are prominent in the negative region of the discharge.

2. Experiments with the hollow (double) cathode discharge

(*a*) *Experimental method*

Apart from measurements of radiation emitted from this type of discharge, previous work has been confined to investigations of the current density as a function of the cathode fall and the pressure, in various gases for cathodes of different shapes. However, there is no information available about the distribution of potential, field or space charge in a hollow-cathode discharge. But since all three quantities are related, it is only necessary to find one of them. It is experimentally convenient to measure the distribution of the longitudinal component of the electric field between the cathodes and calculate the net space-charge density from Poisson's equation and the potential distribution by integration.

The electric field distribution has been found from the deflexion of a feeble beam of electrons which is made to cross the discharge at various points. The method used here is a refinement of that used first (in an abnormal discharge) by Aston (1911) on Thomson's suggestion. The beam does not disturb the discharge as a probe introduced into the dark space would. Recombination, secondary emission, etc., at the probe's surface cannot be avoided, and no reliable data of the space potential can be obtained. The beam method is much more sensitive than that based on the Stark effect in the lines in the emission spectrum. The only objection raised against the use of the beam is that its fast electrons themselves ionize the gas. With the small beam currents used here which are about 10^{-9} A, no appreciable change in ionization of the gas in the discharge is to be expected (see §2(*c*)). Incidentally the field distribution also gives directly the length of the cathode dark space, if the boundary is defined as that point where the extrapolated field has become zero.

The essential improvements on Aston's apparatus are: measurements can be made in discharges at higher pressure, up to 1 mm Hg by using two chambers at different pressure; the electron beam current and accelerating voltage can be independently controlled.

(b) *Apparatus*

The discharge chamber (figure 1), D is a cylindrical glass vessel having four flanges sealed to it at its centre. One pair of these carry the metal bellows supporting the cathodes K_1, K_2, each of which may be moved by means of a calibrated screw attached to the bellows.

The anode A, shown by the broken circle, is behind the cathodes at the end of the cylinder. Its distance from the cathode is such that the discharge is not constricted, but no positive column appears. The electrodes are aluminium disks. Their backs and rims are shielded by glass, as are the cathode supports to prevent the discharge striking.

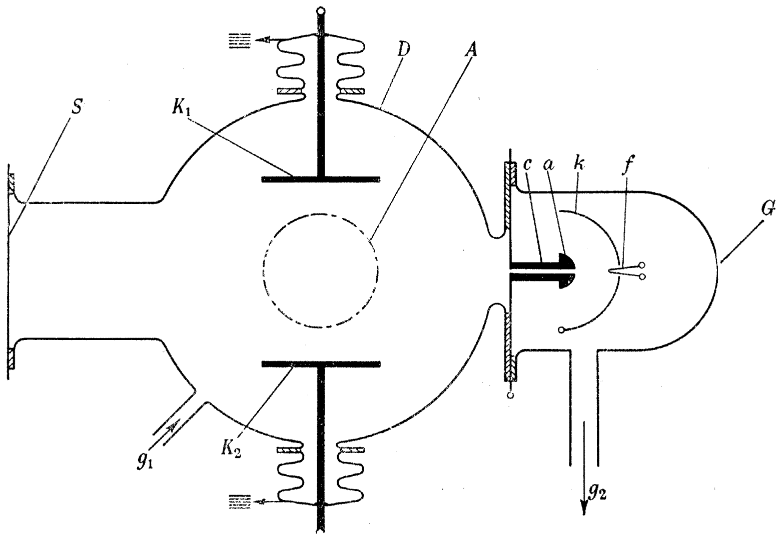

FIGURE 1. Discharge chamber and electron gun; diameter of glass cylinder D, 6 cm; diameter of aluminium cathodes K_1, K_2, 2·4 cm; path length of electron beam between c and S, 12 cm; dimensions of capillary tube c, diameter 0·2 mm, length 2 cm.

The chamber G contains the electron gun which is of the type described by Bricka & Bruck (1948). (The authors are indebted to Dr V. E. Cosslett, Cambridge, for suggesting its use.) The anode a of the gun is a small hemisphere of copper at the end of a steel capillary tube c through which the electrons enter the discharge chamber. The filament f is placed in the converging electric field between a and the concentric copper hemisphere k which is a few hundred volts negative to f. An accelerating voltage between 3 and 12 kV is applied between f and a; the latter is kept at earth potential. By varying the position of k with respect to a, a parallel beam of electrons can be made to pass into D and strike the fluorescent screen S. The position of the spot is measured by means of a graticule on the front of S.

A continuous flow from a cylinder containing pure nitrogen was maintained. Controlled by a needle valve, nitrogen enters D at g_1, passes through c and is pumped off by a mercury diffusion pump at g_2. Therefore, a pressure $p < 10^{-3}$ mm Hg is kept in G, while a glow discharge may be maintained in D at pressures up to 1 mm Hg.

In experiments, K_1 and K_2 are kept at a fixed distance apart. They are then moved together across the path of the beam.

(c) *Possible causes of error*

It was first established that the beam had no effect on the appearance of the discharge, the current or the potential difference across it. Further, the deflexion of the beam was found to be independent of the beam current, when it was varied by a factor 10, and when the accelerating voltage of the beam was varied between 5 and 10 kV the deflexions obtained gave the same result for the field.

So far it has been tacitly assumed that the stray electric field around the discharge is negligible. This is probably not an over-simplification, for the precaution taken in shielding cathodes with glass prevented the discharge spreading. Moreover, ions diffusing out from the discharge are accompanied by equal numbers of electrons; since their density decreases rapidly, only weak fields over short distances can be expected. As will be seen later the good agreement between calculated and measured potentials seems to confirm this supposition.

In order to show that no part of the system receives charges which deflect the beam unpredictably, the beam was deflected by an electrostatic field between the cathodes in the absence of a discharge. The observed deflexions were then compared with those calculated from a theory giving the approximate field distribution between two charged disks. Satisfactory agreement was obtained.

3. Observations and results

At a given pressure p and given inter-cathode distance a, the current density j at the cathode was measured as a function of the cathode fall V_c. In each case the deflexion Δ of the spot was observed for different positions of the cathodes as described in § 2 (*b*). Figure 2 shows graphs for two values of V_c.

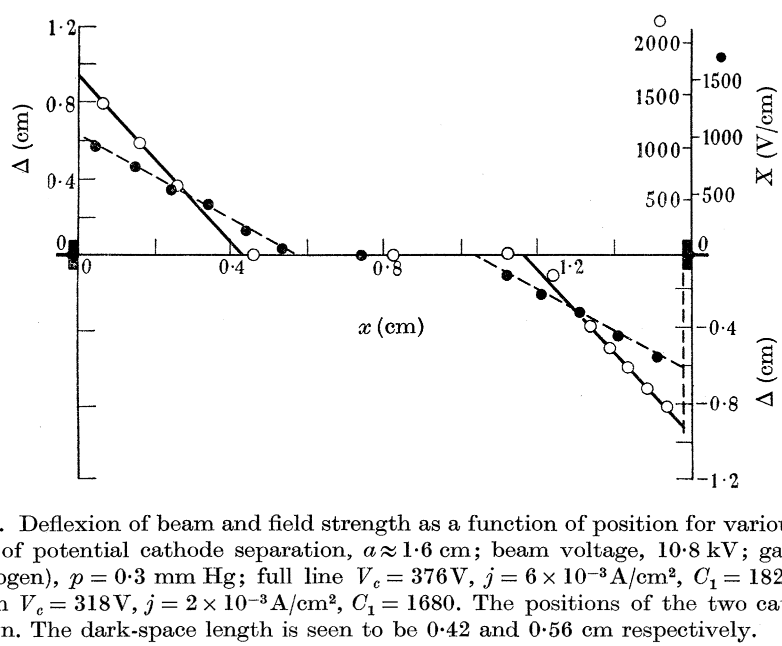

Figure 2. Deflexion of beam and field strength as a function of position for various cathode falls of potential cathode separation, $a \approx 1{\cdot}6$ cm; beam voltage, 10·8 kV; gas pressure (nitrogen), $p = 0{\cdot}3$ mm Hg; full line $V_c = 376$ V, $j = 6 \times 10^{-3}$ A/cm², $C_1 = 1820$; dashed graph $V_c = 318$ V, $j = 2 \times 10^{-3}$ A/cm², $C_1 = 1680$. The positions of the two cathodes are shown. The dark-space length is seen to be 0·42 and 0·56 cm respectively.

It is seen that Δ falls linearly with the distance x from one cathode, and that over the central region no measurable deflexions occur. An increase in V_c increases the slope of the graph in the regions near the cathodes and also increases the length of the central part. It does not, however, introduce any curvature into the graph.

The magnitude of the field X at a distance x may be found from figure 2, since $X = C_1\Delta$ (see §4); values of C_1 are given in the same legend. The length of each dark space d is determined by the point of intersection of the deflexion curve with the x-axis. The remaining distance $(a-2d)$ is regarded as being occupied by the negative glow. Obviously this could be used to determine the 'electrical' length of the glow in a conventional discharge simply by increasing the separation (a) until the current density has fallen to its 'normal' value. It may be added that rough visual observations of d gave results in reasonable agreement with this definition.

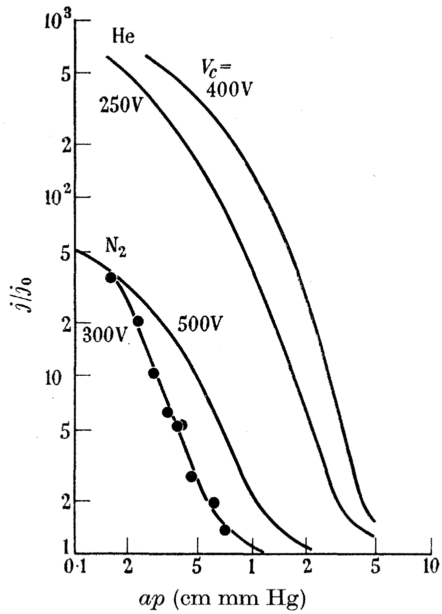

FIGURE 3. Hollow-cathode effect (increase in current density) as a function of the reduced cathode separation for various cathode falls in potential in nitrogen and helium: lowest curve, with aluminium cathodes by authors; remaining curves, with iron cathodes by Güntherschulze (1930).

Curves such as figure 2 have been taken for reduced current densities j/p^2 between 7×10^{-4} and 5×10^{-2} A/cm^2 (mm Hg)^2 and for ap between 0·1 and 1 cm mm Hg. The pressure p was varied between 0·14 and 0·45 mm Hg and a between 0·6 and 1·7 cm. In all these graphs the deflexion is a linear function of the distance. A slight curvature becomes apparent at the boundary between the dark space and the glow only when the dark space is small.

The hollow-cathode effect—the large increase in current density j with reduced cathode separation a—is shown in figure 3 and compared with previous measurements (Güntherschulze 1930). The character of all curves is similar except for the upper part. The curving at large cathode current densities (reduced to the 'normal' current density j_0) is probably due to a heating effect. At large values of j the gas density (and the equivalent pressure) is reduced because the gas temperature increases. This means that the true values of (ap) are smaller and the true values of j/p^2 larger. Because no heating occurs at low current, a density correction for j_0 is unnecessary. The net result is that j/j_0 is higher than the uncorrected value. The difference in cathode materials (iron and aluminium) is not expected to have an effect on the curves. Furthermore, the similarity rules were found to hold, in agreement with earlier observations.

The parameter (ap) which includes the length of the dark spaces and the glow is not a fundamental quantity. However, since the dark-space length d was measured (figure 2), j/p^2 or j/j_0 can be found as a function of pd. Figure 7 shows that j/p^2 is inversely proportional to $(pd)^{\frac{5}{2}}$ approximately. It is interesting to note that at small values of (ap), $j/p^2 \propto (ap)^{-\frac{5}{2}}$, so that $ap \propto pd$ in this range. At large values of (ap) the discharge changes into two independent glow discharges.

It can be seen from figure 3 that the current density depends strongly on the cathode fall. An accurate measurement of this dependence would require a large variation in V_c. This was not possible because of the difficulty in keeping the gas sufficiently cool. The results obtained here suggest

$$\frac{j}{p^2} \propto \frac{V^3}{(pd)^{\frac{5}{2}}}. \tag{1}$$

The values of j must be corrected for the fact that at small values of a the current is not uniformly distributed over the cathodes, being greater at the anode side. The true value of j may be higher by a factor two approximately, for $ap = 0{\cdot}1$, estimated from visual observations.

With the apparatus (figure 1) it was not possible to determine fields below about 50 V/cm, and thus the field near the boundary dark-space glow and in the glow itself could not be measured. In order to obtain greater sensitivity an extension tube of 18 cm length was inserted between S and its flange. This increased the sensitivity fourfold. The highest pressure at which a visible spot could be obtained without increasing the accelerating voltage was now reduced by a factor of about 4.

Figure 4 gives the results of observations near and in the glow of a conventional glow discharge suggesting that the field at the boundary dark-space glow is of order 60 V/cm and falls monotonically to practically zero in the glow. It was not practicable to carry out such observations in the hollow-cathode glow; in this central region the field vector is no longer normal to the cathode surfaces but is directed towards the anode. It is parallel to the cathode surfaces, if the anode is symmetrically placed with respect to the cathodes; moving the cathodes across the beam introduces unsymmetries which cause sometimes reverse deflexions. Such negative fields in the glow have been observed by Emeléus and are still regarded as real (Stein 1953), though Sloane & Emeléus (1931) have later stated that reversed fields are spurious.

It has been thought that a beam of electrons of energy smaller than 10 kV could not be used in gases at pressures greater than 10^{-2} mm Hg because the electrons would be strongly scattered and thus would not produce a well-defined spot on a fluorescent screen. In fact, however, it has been found (Little & von Engel 1952) that it is possible to use electrons of that energy up to a pressure of 1 mm Hg. An explanation of the effect has been given in terms of the ionization produced by the primary electrons; the charges formed diffuse radially outwards and the field accompanying ambipolar diffusion constrains the primaries. This may apply to beam currents of greater than 10^{-5} A, but for the very small currents used here (10^{-8} A) another interpretation must be sought.

Any discussion of this multiple scattering problem must take account of both the most probable angle of scattering at a single collision and the collision cross section. In the experimental results these two parameters appear together and there is uncertainty in isolating either.

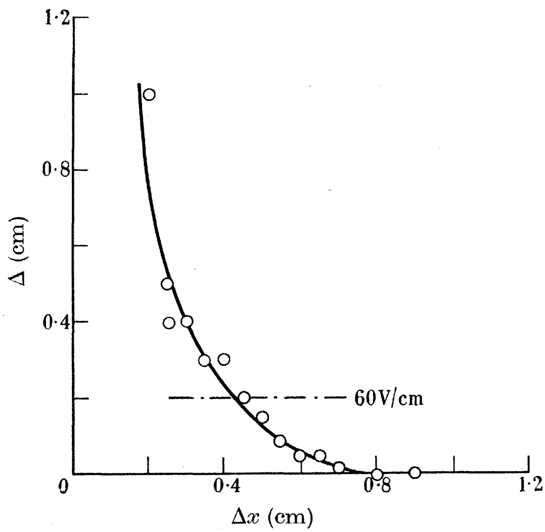

FIGURE 4. Field near the boundary between dark space and glow in a conventional abnormal glow discharge in nitrogen as a function of the distance from an arbitrary zero. $V_c = 460$ V, $i = 5 \times 10^{-4}$ A, $p = 0{\cdot}17$ mm Hg.

The total collision cross-section for electrons in nitrogen has only been measured up to 400 eV. Wave-mechanical theory (Massey & Burhop 1952) gives for the elastic collision cross-section $Q_{\text{el.}}$ at large energy the relation $Q_{\text{el.}} E \approx$ constant, where E is the electron energy. Extrapolating the measurements to 10 keV the values of $Q_{\text{el.}}$ cannot account for the formation of a small spot unless a scattering angle smaller than that obtained from a Coulomb field is assumed. Modern theory, in emphasizing the strong forward scattering of fast electrons, indicates that the Coulomb field acts much further than the actual atomic field (Frazer 1937). This seems to explain the observations. Lenard (1927), using fast electrons in air, had to assume very low collision cross-sections in order to explain the formation of a spot as he postulated Coulomb scattering.

4. The elementary theory of the glow discharge

From graphs such as figure 2 the field may be calculated by the method of Aston (1911). He showed that if the field strength X falls linearly with distance x from the cathode, then the graph of the beam deflexion Δ must also fall linearly. A simple qualitative argument, which will not be presented, indicates that no other field configuration could produce this linear fall in X. To obtain the values of X from the graph of $\Delta = f(x)$, Δ must be multiplied by C_1, a factor given in Aston's paper whose value depends on the gradient of Δ, the beam voltage and geometry.

For the slower electrons used here a correction had to be applied to his calculation, for the beam is deflected into the glow when the field gradient is large. Even so it is still true that Δ need only be multiplied by a constant factor to give the value of X. From this argument it follows that for a dark space of width d, the field at x is given by

$$X/X_c = 1 - x/d, \tag{2}$$

where the electric field strength at the cathode $X_c = 2V_c/d$. The potential V at x with respect to the cathode is then

$$V/V_c = (2x/d) - (x/d)^2. \tag{3}$$

Then the net space-charge density ρ is constant throughout the dark space of a given discharge for

$$\rho = \frac{1}{4\pi}\frac{\mathrm{d}X}{\mathrm{d}x} = \frac{V_c}{2\pi d^2}. \tag{4}$$

These equations express the electrical parameters in terms of d. This result agrees with that obtained on conventional glow discharges with a single cathode (Aston 1911; Geddes 1925; Steubing 1931; Stein 1953). Steubing used instead of the beam the Stark effect, and confirmed the linear fall of field in contrast to earlier observations by Brose (1919) who worked with narrow tubes and found a non-linear fall of field. Probe measurements (Ernst 1935) show a monotonic fall which is steeper at the cathode in contrast to results by Brown & Thompson (1929), but in general measurements with solid probes are not satisfactory. It seems therefore that all reliable methods give a linear dependence of field on the distance and this will be the basis of the following discussion.

Assume that the electron density N^- in the dark space is very small compared with the ion density N^+. Then from (4) we have

$$N^+ = \frac{V_c}{2\pi e d^2}, \tag{5}$$

and thus is constant throughout the dark space.

This shows at once how small the ion current from the glow is, compared with the contribution to the ion current provided by the dark space. Were there a large current from the glow, the ion concentration would fall towards the cathode, contrary to observation, as the drift velocity of the ions increases in larger fields. Hence the ion current from the glow is very small though the opposite view has often been advocated (Emeléus, Brown & Cowan 1934; Druyvesteyn & Penning 1940).

This can be understood if the conditions at the boundary are discussed. Ions may cross the boundary into the dark space by diffusion or motion in the field. Diffusion of ions from the glow into the dark space is inhibited by the presence of electrons in nearly equal concentration. This would still permit ambipolar diffusion at a rate slightly higher than for pure ion diffusion. Even this rate is negligible compared with the ion drift velocity in the field. This field is of order 10 V/cm, but again whatever its precise value the ion drift velocity is less than 1% of the electron drift velocity. Thus the ion current at the boundary is negligible compared with the electron current; since the current at the cathode is carried almost entirely by ions it follows once more that the ion current from the glow makes only a small contribution to the ion current at the cathode.

Nevertheless, the glow is of paramount importance in the discharge. The radiation from the glow together with that from the dark space may release photo-electrons from the cathode. It will be assumed that on the average γ_p electrons are emitted from the cathode when one photon of sufficient energy arrives there. Similarly, each ion reaching the cathode is assumed to release γ_i electrons, but usually $\gamma_i \ll \gamma_p$; metastable atoms act in the same way as photons.

Then at the cathode the electron current density j_c^- consists of three groups of secondary electrons, released by ions and photons from the dark space and photons from the glow

$$j_c^- = \gamma_i j_c^+ + f_d \gamma_p n_d j_c^- + f_g \gamma_p n_g j_g^-, \tag{6}$$

where j_c^+ is the positive-ion current density at the cathode. In the second term representing the electrons released by the photons from the dark space f_d is the fraction of photons which strike the cathode, n_d is the number of photons of energy exceeding the work function produced by one electron and its secondaries in the dark space and j_c^- the electron current density at the cathode. In the third term which describes the effect of photons from the glow, f_g is again a geometric factor and n_g is the number of energetic photons produced by one electron in the glow.

From the argument above $j_g^- = j$, the total current density at the cathode, assuming the same area of discharge cross-section at the cathode and in the glow. With $j = j_c^+ + j_c^-$ we obtain from (6)

$$\frac{j_c^+}{j} = \frac{1-D-G}{1-D+\gamma_i}, \tag{7}$$

where $G = f_g \gamma_p n_g$ and $D = f_d \gamma_p n_d$, being the photon coefficients for the glow and the dark space respectively. It is seen that if G and D are both zero, (7) goes over into the familiar form $j = j_c^+(1+\gamma_i)$. Also, as G or D increase, the fraction of the current caused by positive ions decreases as would be expected. The values of G and D will be discussed later.

But

$$j_c^+ = eN^+ v_c^+, \tag{8}$$

where v_c^+ is the ion drift velocity at the cathode. Then from (5), (7) and (8)

$$\frac{j}{p^2} = \frac{V_c}{2\pi (pd)^2} v_c^+ \frac{1-D+\gamma_i}{1-D-G}. \tag{9}$$

It is necessary to discuss the variation of v_c^+, γ_i, G and D with the discharge parameters in order to obtain an expression which can be compared with experiment; γ_i and γ_p in this elementary treatment may be considered constant. Already, however, it can be seen from (9) that j/p^2 increases rapidly with decreasing pd when V is constant, even if the influence of the accompanying changes in v_c^+, γ_i and γ_p is neglected.

5. Motion of the positive ions in the dark space

The positive ions which originate in the main from the boundary glow/dark space move to the cathode in an electric field of ever-increasing strength. It is known that when in equilibrium with a uniform field positive ions have a drift velocity which is either proportional to the reduced field X/p or to $(X/p)^{\frac{1}{2}}$ according to whether the field is weak or moderate (Munson & Tyndall 1941). The measurements with ions in their molecular gas extend up to values of X/p of several hundred.

All attempts to use these results even in a modified form to allow for the non-uniform field have proved to be unsuccessful (Lunt *et al.* 1941). The reason for this failure was originally thought to be the lack of equilibrium in the non-uniform field. Calculations based on classical scattering (which are not given here) allowing for incomplete equilibrium show that the ion energies at the cathode have a distribution with a maximum about 10 % V_c. This is in contradiction to the work by Chaudrhi & Oliphant (1932) and Campan (1934), who found the maximum between one-third and one-half of the cathode fall which was between 200 and 2000 V the higher the larger V_c. Some ions had even energies equal to V_c. It must be concluded that classical treatment cannot be applied here.

The present trend is to regard charge transfer as the main non-classical process in the theory of ion mobilities. An encounter between an ion which has been accelerated and a molecule of the same gas results in a transfer of an electron from the molecule to the ion but kinetic energy is not exchanged. After the encounter a fast neutral molecule proceeds in the field direction and a slow positive ion of thermal energy moves away initially in a direction about 90° to the field (Massey & Burhop 1952). The slow ion is soon accelerated in the field direction. This series of events is equivalent to a positive ion losing all its kinetic energy and starting from rest after the collision. Therefore any ion which strikes the cathode could only have an energy acquired along the last free path after a charge transfer collision. The reverse process by which the fast neutral molecule is ionized can be neglected here. The energy gained in one such free path could be a large fraction of V_c if it could be shown that an ion can retain its energy in a succession of elastic collisions between the last charge transfer collision and the instant when it strikes the cathode.

The wave-mechanical treatment of the elastic scattering of atomic ions in their own gas reveals that the main contribution to collision cross-section comes from ions scattered into angles less than 5° for ions of energy < 1 eV; forward scattering is more likely as the ion energy rises. One can safely apply these results to the case of molecular ions in their own gas because the molecular nature hardly affects the angular distribution of scattering. Experimental confirmation may be found from atomic beam studies (Fraser 1937). A consequence of this small-angle scattering is that the energy of the incident ion cannot be much reduced by such an encounter. Therefore an ion which moves from the glow to the cathode will be able to pick up energy up to V_c unless it makes a collision in which a transfer of charge occurs. It has been shown (Simons, Fontana, Francis & Unger 1943) that at low energy charge-transfer neutralization cross-sections decrease with increasing ion energy; thus it is to be expected that near the boundary of the dark space where the fields are low, much charge transfer will occur. It is obvious now that any argument which is based on the assumption that the random velocity of ions exceeds the drift is doomed to failure. To give a simplified picture, the ions move near the cathode as an ion beam, near the glow as an ion swarm; in the beam the drift velocity is large compared with the random velocity, but in the swarm the reverse is true.

The energy of the ions arriving at the cathode is then determined by the cross-section for charge transfer. Since from measurements in nitrogen by Wolf (1937) and by Simons *et al.* (1943) in hydrogen it appears this cross-section Q_{+0} decreases only slowly with increasing energy. It will be assumed here for simplicity that it is constant in nitrogen and that exchange of charge occurs once in four elastic collisions, so that $Q_{+0} = 1/\lambda_{+0} = 70\,\mathrm{cm^2/cm^3}$ at $p = 1$ mm Hg.

Since the potential at any point is known from equation (3), it follows that the velocity v_c^+ of the ions arriving at the cathode is

$$v_c^+ = \left[\frac{2eV_c}{M}\left\{\frac{2\lambda_{+0}}{pd} - \left(\frac{\lambda_{+0}}{pd}\right)^2\right\}\right]^{\frac{1}{2}}, \tag{10}$$

where M is the ion mass and e the ion charge. This result will be used later.

6. The influence of the negative glow

In order to assess the importance of the negative glow, it is necessary to know the rate of production of photons in the glow and the photo-electric yield at the cathode (Laszlo 1932; Kenty 1933; Wainfan, Walker & Weissler 1953). The number of electrons released from metal surfaces by photons of energy between about 10 and 20 eV is nearly independent of the photon energy, and the yield γ_p is of the order 10^{-1} electron per incident photon if the surface is not degassed.

The number n_g of photons emitted from the glow per electron entering it is given by the number of photons produced by one fast electron times the fraction f of fast electrons. Let ηV photons be produced by a fast electron which loses all its energy in the glow V. Now this number is taken to be of the same order but larger than the number of ions produced by one fast electron. It is known (von Engel & Steenbeck 1932, p. 41) that an electron with an initial energy V of a few hundred electron-volts produces $V/70$ ion pairs in nitrogen when it loses all its energy.

Let the fraction f of the electrons be those which enter the glow with an energy > 100 eV for nitrogen and > 50 eV for helium. Assuming that the fast electrons have energies which correspond to the space potential V in the dark space, then all electrons coming from a certain distance y from the glow will have energies > 100 eV. This distance is found from (3) to be

$$y/d = \sqrt{(100/V_c)}.$$

Since electrons multiply from the cathode ($y = d$) to y, the number of fast electrons entering the glow per electron from the cathode is

$$\bar{s}d\{1 - \sqrt{(100/V_c)}\},$$

where $\bar{s}$ is the average ionization coefficient in the dark space. The number of electrons released from the cathode by photons from the glow is thus

$$j_c^- f_g \gamma_p \exp\left[-\bar{s}d\{1 - \sqrt{(100/V_c)}\}\right] \eta b V_c = G j_g^-, \tag{11}$$

where $b < 1$ and bV_c is the average energy of the fast electrons. Equation (11) defines G in (9) as $j_g^-/j_c^- = \mathrm{e}^{\bar{s}d}$.

The value of f_g and its variation in the conventional and hollow-cathode discharge will be discussed later.

To regard the glow as a source of short-wave radiation would, according to Emeléus (1935), account for the properties of the Faraday dark space.

7. Excitation in the dark space

There remains to be determined the quantity D in (9). It depends on n_d, the number of high-energy photons produced per electron in the dark space. No information is available and thus only an estimate can be made. However, this is admissible, as D appears as the least important term in (9). Assuming that the number of such photons is about the same as the total number of ions in the dark space

$$n_d \approx (\bar{s}/p)\,(pd). \tag{12}$$

For example, in nitrogen for single collisions the number of ions per centimetre is less than 10. In general,

$$D = f_d n_d \gamma_p = f_d(\bar{s}/p)\,(pd)\,\gamma_p, \tag{13}$$

where f_d will be taken to be 0·5 for the conventional glow discharge with one cathode and 1 for the hollow-cathode discharge.

8. Final results

Substituting from equations (10), (11) and (13) into (9) one obtains (in e.s.u.)

$$\frac{j}{p^2} = \left(\frac{e\lambda_{+0}}{\pi^2 M}\right)^{\frac{1}{2}} \frac{V_c^{\frac{3}{2}}}{(pd)^{\frac{5}{2}}} \left(1 - \frac{\lambda_{+0}}{2pd}\right)^{\frac{1}{2}} S(\gamma), \tag{14}$$

where the secondary process function

$$S(\gamma) = \frac{1 - f_d \gamma_p(\bar{s}/p)\,(pd) + \gamma_i}{1 - f_d \gamma_p(\bar{s}/p)\,(pd) - f_g \gamma_p \eta b V_c \exp\{-\bar{s}d\,\sqrt{(100/V_c)}\}}.$$

This equation should hold for all discharges with plane cathodes in any gas, whether these are normal or abnormal discharges with a single cathode, or hollow-cathode discharges with two cathodes.

Applying (14) to a normal glow discharge it is seen that since V_c, λ_{+0} and pd are given for a given gas, j/p^2 will depend on γ_p, that is, on the photo-electric yield of the surface for the 'active' photons with a gas present. However, $S(\gamma)$ is here only a correction term and hence j/p^2 should not depend much on the cathode material; this is in agreement with observations (von Engel & Steenbeck 1934, vol. 2). For a given cathode gas with a large dark space should have a low value of f/p^2, and this is so, for example, in helium.

When the discharge becomes abnormal, it is known that as V_c increases pd decreases. Hence j/p^2 will rise rapidly with V_c as is observed. The influence of the other terms containing λ_{+0}, pd and $S(\gamma)$ is not very strong.

The conditions are different in hollow-cathode discharges. First of all, the geometric factors f_d and f_g which were $< \frac{1}{2}$ for the open discharge are now ≈ 1. This affects the photon contribution from the dark space which occurs both in the numerator and denominator of $S(\gamma)$, but the main influence is through the glow. Thus $S(\gamma)$ increases if f_d and f_g rise. When V_c is kept constant and the separation a is reduced, pd decreases. The most important terms containing pd in (14) are the $(pd)^{\frac{2}{3}}$ term and the exponential term in $S(\gamma)$, both of which cause j/p^2 to rise when pd falls.

This formal explanation of the hollow-cathode effect is easily interpreted physically; by reducing the separation between the cathodes, the dark space is compressed. Since V_c is maintained, the field gradient becomes steeper and the ion density rises. At the same time the potential difference over the last free paths of ions striking the cathode is increased and so is their velocity at the cathode. Because of the larger ion velocity and concentration the ion-current density at the cathode is greatly increased. Moreover, the electrons lose less energy in the shorter dark space and more in the glow by ionization and excitation; the stronger light from the glow increases the photo-electric emission from the cathodes. As a result of this the electron current density will rise too.

The rate of ionization in the dark space will also be increased by electrons which penetrate the glow and emerge into the opposite dark space with considerable energy (see below).

It may be thought that the factor $S(\gamma)$ is not essential to any of the explanations given. However, a consideration of the condition of the steady state—that one electron starting at the cathode must produce a sufficient number of ions and photons to release one electron from the cathode again—shows that photo-electric processes must be included. This was tentatively suggested by Lompe, Seeliger & Wolter (1939); see also Geiger (1937) and Weizel & Olmesdahl (1939).

In this way $j/p^2 = f(V_c)$ and $pd = f(V_c)$ can be found for a conventional discharge. Ignoring for simplicity production of ions and photons in the dark space, the discharge is considered to be maintained by photons from the glow. From the arguments leading to (11), this condition

$$Ge^{\bar{s}d} = f_g \gamma_p \eta b V_c \exp\left[\bar{s}d\{1-\sqrt{(100/V_c)}\}\right] = 1. \tag{15}$$

From (15), because $\bar{s}d = (\bar{s}/p)(pd)$,

$$pd = \frac{1}{(\bar{s}/p)\{1-\sqrt{(100/V_c)}\}} \ln \frac{1}{f_g \gamma_p \eta b V_c}. \tag{16}$$

However, f_g decreases as V_c increases because the length of the glow increases (Brewer & Westhaver 1937) and therefore the centre of photon production recedes from the cathode. For nitrogen and other gases it was found that length of the glow is approximately proportional to V_c. It is assumed in what follows that $f_g V_c =$ constant, which is consistent with the strong scattering and absorption in nitrogen (Weissler, Lee Po & Mohr 1952). The constant is found to be equal to 110 from the condition that $f_g = 0{\cdot}5$ when the glow is as short as possible that is in a normal discharge. With $\gamma_p = 0{\cdot}2$, $\eta b = \frac{1}{50}$ (which means 50 eV per photon) and $\bar{s}/p = 8$ ion pairs per cm per electron in the dark space, figure 5 is obtained from (16). The measured values agree sufficiently well with those predicted. In other gases the curves are similar, and thus an equation of the type (16) should give a reasonable figure. Equation (16) gives the observed rapid fall in pd just above the normal V_c as well as the nearly constant pd at large V_c.

This simple treatment ignores entirely the secondary electron emission at the cathode due to ions and photons from the dark space and also that due to photons produced in the glow by slow electrons from the dark space and by electrons which gain energy in the field of the glow. It is a complete departure from traditional assumptions that ions alone are important in maintaining the discharge. The crude

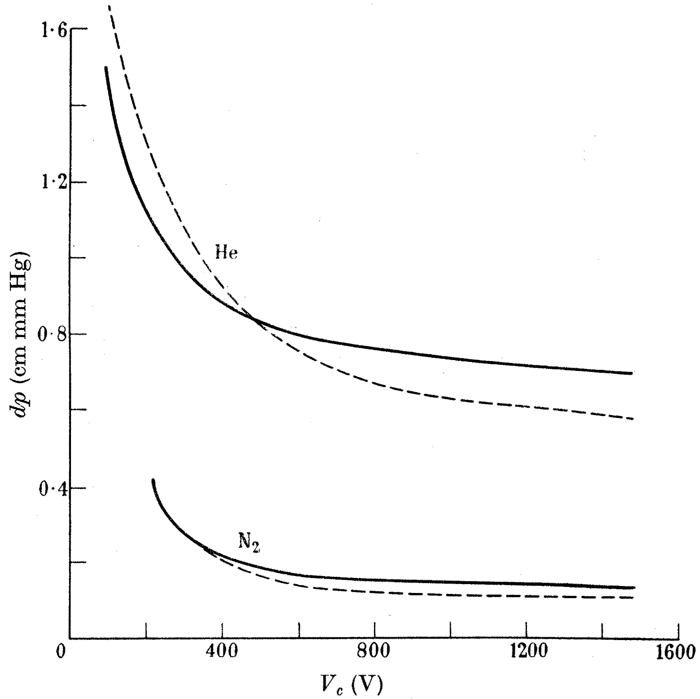

FIGURE 5. Reduced cathode dark space as a function of the cathode fall for a conventional glow discharge with iron cathode. ----, Experiment (Güntherschulze 1930); —, theory. For nitrogen: $f = 110$, $\gamma = 0{\cdot}2$, $\eta b = 1/50$; for helium: $f = 75$, $\gamma = 0{\cdot}3$, $\eta b = 1/40$.

approximations made show that by including the ultra-violet radiations from the glow in the condition for maintenance, the contraction of the dark space in an abnormal discharge may be easily derived. In a conventional discharge (16) states that pd is larger the lower $\bar{s}/p$; this is borne out by comparing, for example, helium with nitrogen. For helium $pd = 1{\cdot}7$ cm mm Hg and $\bar{s}/p \approx 1$, whereas in nitrogen $pd = 0{\cdot}3$ and $\bar{s}/p \approx 8$.

Using (16), (14) may be simplified if only the contribution of the photons from the glow to $S(\gamma)$ is considered and if the third term in (14) is taken as unity, one obtains (in e.s.u.)

$$\frac{j}{p^2} = \left(\frac{e\lambda_{+0}}{\pi^2 M}\right)^{\frac{1}{2}} \frac{V_c^{\frac{3}{2}}}{(pd)^{\frac{5}{2}}} \frac{1}{1-\mathrm{e}^{-\bar{s}d}}. \tag{17}$$

Figure 6 shows $j/p^2 = f(V_c)$ for nitrogen and helium in the open discharge. The values of pd are taken from (16) and λ_{+0}/M for He_2^+ and He^+ are assumed equal. The agreement is as good as can be expected.

In the hollow-cathode discharge equation (17) may still be applied, for the net space-charge density in the dark space is constant here as in the open discharge. However, (16) cannot be used, for the value of pd is determined by the cathode separation ap as well as the cathode fall V_c.

Those fast electrons which have not lost their energy in crossing the glow may penetrate into the opposite dark space where they move against the field until their drift velocity has become zero. They are subsequently accelerated towards the glow, excite and ionize molecules along their path and contribute to the multiplication

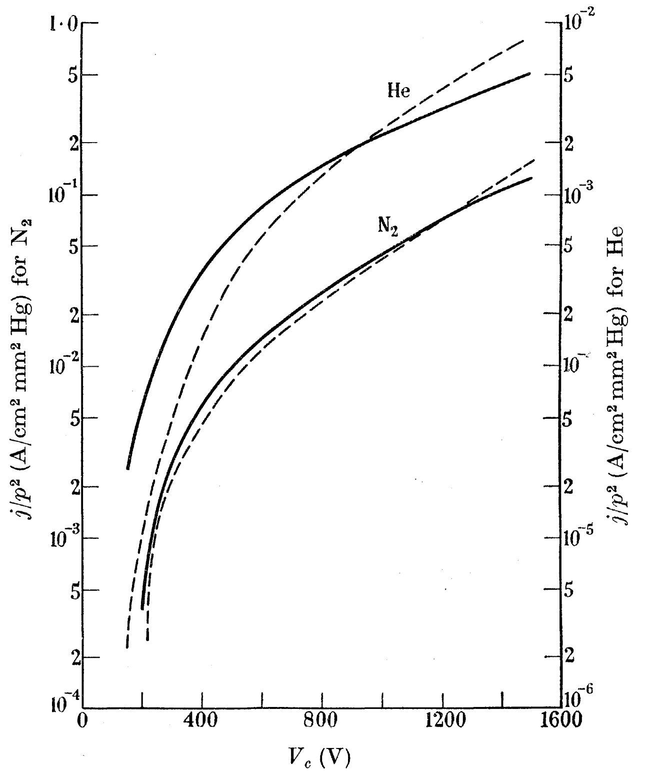

FIGURE 6. Reduced current density as a function of the cathode fall for a conventional glow discharge with iron cathode. ----, Experiment (Güntherschulze 1930); —, theory.

of charges as well as to photons of high energy (von Engel & Steenbeck 1934, p. 114). Therefore as ap decreases $\bar{s}/p$ increases; if $\bar{s}/p \propto 1/ap$ for $ap < 0{\cdot}4$, the observed proportionality between (pd) and (ap) (§3) follows from (16).

Moreover, of the photons produced, whether in the dark space or the glow, nearly all reach the cathodes so that $f_g \approx 1$. For a hollow-cathode discharge then at $ap < 0{\cdot}4$ with V_c in volts

$$pd = \frac{ap}{3} \frac{1}{1-\sqrt{(100/V_c)}} \ln \frac{1}{f_g \gamma_p \eta b V_c}, \tag{18}$$

if $\bar{s}/p = 8$ at $ap = 0{\cdot}4$. With reasonable values for the parameters, (18) gives the correct absolute magnitude of pd. No more than this can be stated in view of the uncertainties in the constants. Equation (18) shows also that pd is very sensitive to variations in V_c, since the log term is near unity. It follows that j/p^2 increases rapidly with V_c which is a striking feature of the hollow-cathode discharge.

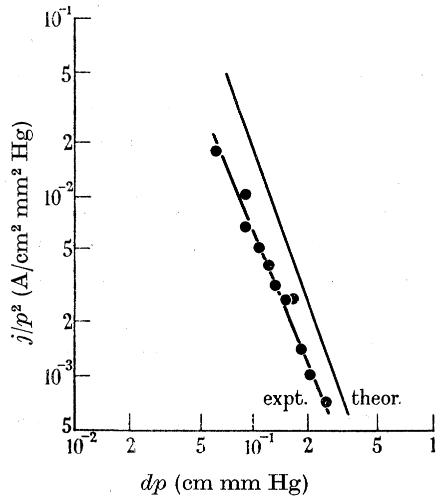

FIGURE 7. Reduced current density as a function of the reduced cathode dark space for a hollow-cathode discharge in nitrogen with aluminium cathodes. $V_c = 300$ V.

When the observed pd is substituted in (17) for given V_c, j/p^2 as a factor of pd is found (figure 7). The agreement with experiment is again satisfactory, bearing in mind the correction to the experimental values of j/p^2 due to non-uniform current distribution (see § 3). The elementary theory given here does not take account of the action of metastable molecules which may ionize the gas by pair collision (Oldenberg 1953) or extract electrons from the cathode.

It is interesting that Druyvesteyn & Penning (1940) showed that the electrons deliver most of their energy to the glow (see also Brewer & Westhaver 1937). However, they assumed that the energy was spent in ionization, providing an ion current from the glow. This has been shown above to be untenable.

The discharge current in the glow is carried almost entirely by electrons, as it is at the boundary. Since j^- well in the glow is given by the concentration N^- and the drift velocity v^- (Loeb 1939), the upper limit of X/p can be estimated. With N^- about equal N^+ in the dark space (10^9 to $10^{10}/\text{cm}^3$) X/p is 10 V/cm mm Hg or less. This is comparable with the field in the positive column.

9. Conclusions

The agreement between theory and observations over such a wide range of conditions for various gases and cathode systems makes it essential to discuss the radiation in the discharge. In particular is there sufficient evidence available to justify the emphasis placed on ultra-violet radiation from the glow?

As to the existence of such radiation Wiedemann (1895) was probably the first who when observing thermoluminescence suspected some kind of radiation to be produced in the discharge, and Dauvillier (1926) provided conclusive evidence of the emission of radiation even from the dark space. This radiation decreases in wave-length the nearer the emission centre is to the glow. Further, the glow itself emits radiation whose wave-length decreases as the pressure decreases. At about 0·1 mm Hg it is of the order 50 Å, corresponding to a quantum energy of 240 eV, whereas at higher pressures the wave-length is of the order 1000 Å. In fact hollow-cathode discharges are widely used spectroscopic sources of ultra-violet light. There is no doubt that radiation from the discharge has enough energy to release photo-electrons from any cathode surface (see Thomson & Thomson 1933).

It remains to be shown that the intensity of radiation is sufficient to influence the discharge markedly. Dember & Gehlhoff (1906) found that the cathode fall for a discharge in helium with a potassium-sodium cathode was reduced from about 200 to 100 V when the cathode was irradiated with light from an arc lamp. With strong abnormal discharges no change was observed. This indicates that the irradiation was comparable with that due to the glow in a normal discharge but smaller than the light from the glow in strong abnormal discharges. Costa (1939) showed that photo-emission from a subsidiary cathode occurs when radiation from an electron swarm is incident upon it.

It appears therefore that the glow is a prolific source of ultra-violet radiation which is a major factor in the maintenance of glow discharges.

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