

NON-EQUILIBRIUM IONIZATION GROWTH IN MOLECULAR HYDROGEN

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Summary

A thin-film cathode is used in an examination of the spatial growth of ionization in molecular hydrogen at high values of the parameter E/p (E is the electric field strength in V/cm; p is the gas pressure in torr at 0°C). Particular attention is given to the region of small gap separations d where non-equilibrium ionization growth occurs. The effect of non-uniformity of the electric field in this region due to anode perforations is demonstrated and the consequences of including ionization current measurements at small values of d in analyses of growth of current measurements are discussed. The variation of the "effective" Townsend coefficient a/p with E/p in uniform field conditions is obtained for values of E/p up to 1000 V cm⁻¹ torr⁻¹.

I. INTRODUCTION

Recent investigations of the pre-breakdown growth of ionization in molecular hydrogen in crossed electric and magnetic fields (Fletcher and Haydon 1965; Haydon 1965) indicate that above electron energies of approximately 5 eV the momentum transfer cross section in hydrogen falls rapidly. In the collision interaction between electrons and neutral molecules a marked scattering of the electrons then occurs in the forward direction and the concept of a "swarm" of electrons moving through the gas with a mean energy appropriate to some spatially independent electron energy distribution becomes questionable. A gradual transition from "swarm" to "beam" characteristics would be expected as the effects of forward scattering become increasingly important. In terms of the experimental parameters appropriate to pre-breakdown studies, this means that the larger the value of E/p (where E is the electric field strength and p the gas pressure at 0°C), and the smaller the value of B/p (where B is the transverse magnetic field strength) then the more important will the beam characteristics become. The lower the pressure the higher is E/p for a given applied uniform field strength, so that these non-equilibrium effects should control the preparation of plasmas at the low pressures of interest in many plasma physics studies.

Unfortunately a clear understanding of the problem has failed to emerge despite investigations over many years. There is, for example, a complete lack of agreement about the significance of, and actual values for, the primary and secondary ionization coefficients in molecular hydrogen at values of $E/p \geq 200$ V cm⁻¹ torr⁻¹. Although some effects of impurities and a number of other problems associated with pre-breakdown studies at large E/p values have been discussed by Haydon and Robertson (1961), several other investigations have been reported since then (Chanin and Rork 1963; Golden, Nakano, and Fisher 1965) that indicate that the pre-breakdown ionization growth is not well understood. Specifically there appears to be

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a discrepancy of some 60% in the value of a/p quoted for $E/p = 350 \text{ Vcm}^{-1} \text{ torr}^{-1}$ in hydrogen. The present paper is concerned with this non-equilibrium ionization and reports recent measurements in molecular hydrogen that also extend investigations of certain aspects of the problem associated with ionization in non-uniform electric fields (Haydon and Robertson 1961).

II. THE SPATIAL GROWTH OF IONIZATION

(a) *Equilibrium Conditions at Low Values of E/p*

When swarm conditions prevail with a spatially independent electron energy distribution, the ionization current in a uniform electric field between electrodes distance d apart is given in terms of the primary (a/p) and secondary (ω/a) coefficients by

$$I = \frac{I_0 \exp ad}{1 - (\omega/a)(\exp ad - 1)}, \quad (1)$$

where I_0 is the initial electron current from the cathode produced by some external agency and both a/p and ω/a are independent of d . In hydrogen this equation is satisfactory for values of $E/p \leq 100$ and analyses of I, d measurements by many investigators show very good agreement.

(b) *Non-equilibrium Conditions at Moderate Values of E/p*

As E/p increases, the mean energy of the electrons released from the cathode and contributing to the initial current I_0 is very much less than the mean energy of the electron swarm that develops when equilibrium is achieved at some distance from the cathode. In order to take this non-equilibrium region into account in analysing I, d measurements, Kruithof and Penning (1936, 1937) introduced a distance d_0 through which the electrons must fall before reaching equilibrium. The growth equation then becomes

$$I = \frac{I_0 \exp a(d-d_0)}{1 - (\omega/a)\{\exp a(d-d_0) - 1\}}. \quad (2)$$

The interpretation of the term d_0 and methods for analysing this equation have been discussed elsewhere (Jones and Llewellyn Jones 1958; Haydon 1963). In these laboratories a method in which the reciprocals of I at values of d (Y_d) are plotted against reciprocals of I at values of $d + \Delta d$ ($Y_{d+\Delta d}$) has been adopted (Gosseries 1939). If equilibrium conditions prevail at all values of d , these plots should yield a family of straight lines corresponding to different values of Δd , but each slope ($\exp a\Delta d$) should give the same value of a .

Any curvature in these plots of Y_d versus $Y_{d+\Delta d}$ in the region of small electrode separations would indicate that some or all of the coefficients a , ω , and I_0 are dependent on electrode separation d . This would arise if $d \leq d_0$ and the electrons have not reached an equilibrium energy distribution. On the other hand, the perforations in the anode electrode through which ultraviolet light is usually admitted to the cathode may distort the otherwise uniform applied electric field at small electrode separations. Electrons would then move in a non-uniform electric field and

the magnitudes of both α and ω may then depend on d , especially if d were sufficiently small. These situations arise typically at $E/p = 100$, where a downward curvature is observed at small values of d and is attributed to the effects of the non-equilibrium region ($\equiv d_0$), and at $E/p = 800$, where the upward curvature observed is associated with non-uniform electric fields at small separations. This is discussed in more detail in Section V.

(c) *Non-equilibrium Conditions at Large Values of E/p*

When the non-equilibrium distance d_0 effectively extends over the whole inter-electrode spacing, both α and ω may be functions of distance. The ionization growth equation then becomes

$$I = \frac{I_0 \exp\left(\int_0^d \alpha dx\right)}{1 - \int_0^d \omega \exp\left(\int_0^x \alpha dx\right) dx}. \quad (3)$$

The corresponding Gosseries-type equation becomes

$$Y_d = Y_{d+\Delta d} \exp\left(\int_d^{d+\Delta d} \alpha dx\right) + \frac{\left\{\int_d^{d+\Delta d} \omega \exp\left(\int_0^x \alpha dx\right) dx\right\} \exp\left(-\int_0^d \alpha dx\right)}{I_0}, \quad (4)$$

which reduces to the equilibrium form

$$Y_d = Y_{d+\Delta d} \exp a\Delta d + Q(\exp a\Delta d - 1), \quad (5)$$

where $Q = (\omega/\alpha)/I_0$, only when α and ω are independent of d .

In general the actual Y_d versus $Y_{d+\Delta d}$ plots for equation (4) become a family of curves, and some knowledge of the functional relationships of both α and ω with electrode separation is required for a full interpretation of the growth equation.

III. PREVIOUS INVESTIGATIONS

Early measurements of α/p in hydrogen by Ayres (1923) and Hale (1939) showed a lack of agreement, which Hale attributed to mercury contamination of Ayres's hydrogen samples. Rose (1956) examined this aspect in particular, but the values he quoted for pure hydrogen were shown by Jones and Llewellyn Jones (1958) to be incorrect at high E/p because of the neglect of secondary ionization in the analysis. Blevin, Haydon, and Somerville (1957) confirmed that impurities were unimportant at low E/p and Haydon and Robertson (1961) showed that the Gosseries (1939) analysis should be used at high values of E/p . Also, values quoted by Davies and Milne (1959) at $E/p \sim 350$ were shown to be high, probably because of vapour contamination of their gas samples. Haydon and Robertson also drew attention to both non-equilibrium effects at small gap separations and the possible effects of electric field distortions.

Although Fletcher and Davies (1963) substantially confirmed the values of Haydon and Robertson, Chanin and Rork (1963) reported much higher values. In a more recent paper Golden, Nakano, and Fisher (1965) report new measurements of α/p made in Rose's original ionization chamber. They also indicate their definite

preference for Rose's original "high" values. In particular they invoke a computerized analysis of their measurements in support of the Rose values and appear to attach little significance to a number of problems raised in earlier papers.

In attempting to clarify the situation, we have used the analytical approach of Gosseries (1939), which shows clearly the effects of changes of various parameters. We have investigated in detail the situation at $E/p \geq 350$, where the discrepancies reported are well outside any experimental error. Particular attention has been given to measurements corresponding to small gap separations, where not only is the experimental accuracy decreasing, but where non-equilibrium effects first begin to appear.

Haydon and Robertson (1961) examined the effects of anode holes and showed that self-consistent values for the ionization coefficient α/p can only be obtained provided that measurements made in the small d , distorted-field region are not included in the analysis. Furthermore, the effects of this region on the measurements increases with increasing size of the anode holes and decreasing electrode separation. Since smaller electrode separations are used at higher pressures, these field distortion effects should be greater the higher the pressure used in the investigation. For instance, Chanin and Rork quote a pressure of 4.3 torr at $E/p = 500 \text{ V cm}^{-1} \text{ torr}^{-1}$ and measurements were made at separations as low as 0.01 cm.

The use of these extreme conditions has led us to examine the non-equilibrium region in greater detail using the electrode arrangements and techniques described below.

IV. EXPERIMENTAL DETAILS

The ionization chamber contained two Rogowski-profiled copper electrodes with flat centre sections 5 cm in diameter. The electrodes were parted at the edge of the flat surface and the resultant guard rings, G (see Fig. 1), were insulated from the respective centre electrodes by sapphire mounting rods. The electrode separation could be adjusted and measured by use of a micrometer screw gauge attached externally to copper bellows. Ultraviolet light from a quartz high pressure mercury vapour lamp (Hewittic, type 547C) passed through a quartz window set behind electrode A and was incident on the back of the centre electrode C. This centre electrode could be unscrewed to allow various types of centres to be used. The electrode assembly was mounted inside a vacuum envelope, which was pumped and filled with hydrogen gas using the same vacuum techniques described in an earlier paper (Haydon and Robertson 1961).

Initially, the central section of the anode contained forty-nine 0.5 mm holes drilled within a circular area of 1 cm diameter at the centre. This centre section was subsequently replaced by a copper disk from which a circular central section 0.4 cm in diameter had been removed and replaced by a fine phosphor-bronze mesh (100 lines/in.) set flush with the front surface. This allowed the initial photoelectric current to be generated by the ultraviolet light incident on D, which was then used as the cathode. Later C was replaced by a copper annulus 5 cm in external diameter and 3 cm in internal diameter into which a quartz plate was set flush to the front

surface. A thin film of metal (thickness $\simeq 1000 \text{ \AA}$) was vacuum deposited onto the front surface of this electrode. The initial photoelectric current was then produced by electrons emitted into the ionization region when the back surface of this film was irradiated by ultraviolet light. In this configuration, electrode C acted as the cathode. Initial photoelectric currents were typically of the order of 10^{-12} A and at no time were the ionization currents in excess of 10^{-8} A . Ionization currents were measured to an accuracy of 2% with a Vibron 33C electrometer.

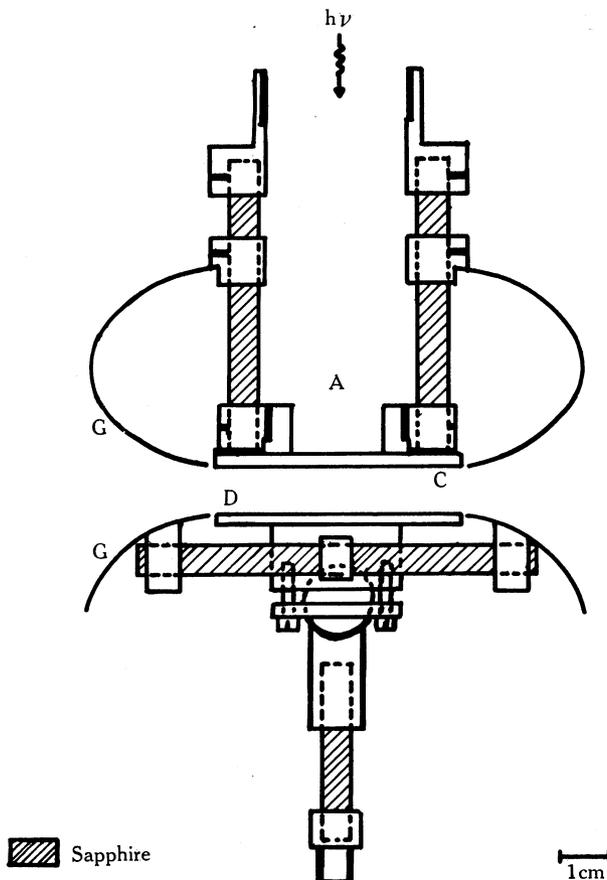


Fig. 1.—Electrode assembly.

V. RESULTS

Measurements were first made with the phosphor-bronze mesh electrode, because these conditions more nearly corresponded to the conditions of Chanin and Rork's experiment. However, we were still able to confirm our own values of a/p at $E/p = 350$ and to show that only when measurements at the lowest separations are included in a three-point analysis are much larger values obtained.

Detailed investigations were then made in which the following parameters were varied:

- (1) cathode material (copper, nickel),
- (2) anode material (copper, nickel, carbon, phosphor-bronze),
- (3) magnitude of I_0 ($\sim 10^{-13}$ to $\sim 10^{-10}$ A),
- (4) guard electrode potentials (varied from zero to anode potential),
- (5) gas pressure (0.5 to 5 torr).

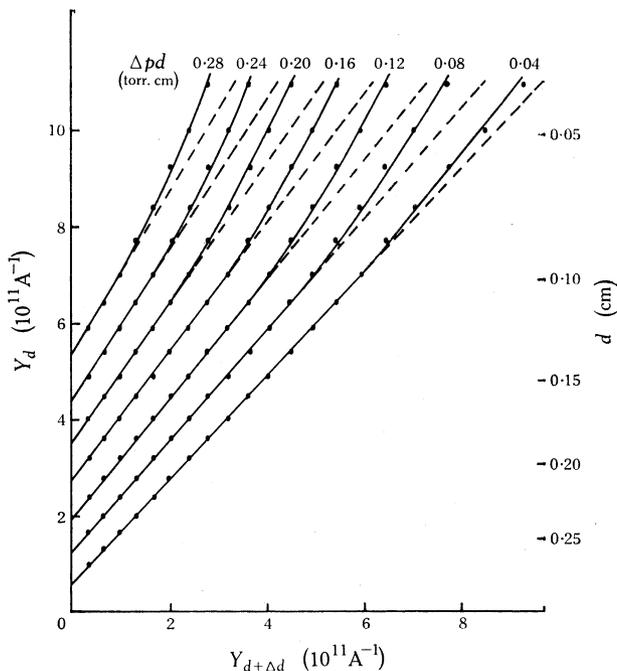


Fig. 2(a).—Family of Gosseries plots Y_d versus $Y_{d+\Delta d}$ for $E/p = 800$ $\text{V cm}^{-1} \text{ torr}^{-1}$ ($p = 1.64$ torr) using a mesh anode and a solid cathode. Values of electrode separation d for corresponding values of Y_d are also given. Curvature appears at $d \leq 0.10$ cm. The effective value of a/p (from slope $\exp a\Delta d$ of linear portion) is 1.85.

In all cases high values of a/p at $E/p = 350$ could not be obtained unless measurements at very small separations were included in the analysis. Outside the region of non-equilibrium, Gosseries plots were always self-consistent, yielding a value for a/p within the range 2.60 ± 0.1 at $E/p = 350$.

In the past the non-equilibrium region has been inadequately understood, the curvature in the Gosseries plots being in part due to the d_0 effect and in part due to the non-uniform field effects produced by the anode perforations. In order to separate these effects, the thin-film techniques described above were used. These films were sufficiently thick to retain essentially the same properties of the bulk electrode material and yet thin enough for the electrons to be released into the ionization region when the back surface of the film was irradiated with ultraviolet

light. With this arrangement it was possible to explore the growth of currents in an essentially uniform electric field down to much smaller electrode separations than was previously possible. Curvature did not appear in the Gosseries plots for measurements at $E/p = 350$ and the value of a/p was again 2.6 ± 0.1 . The effect of the change to thin-film techniques is most spectacular at the larger values of E/p . For instance, Figure 2 shows for comparison Gosseries plots with anode perforations (Fig. 2(a)) and with thin-film techniques (Fig. 2(b)). In each case the values of electrode separation d corresponding to values of Y_d are also shown, from which

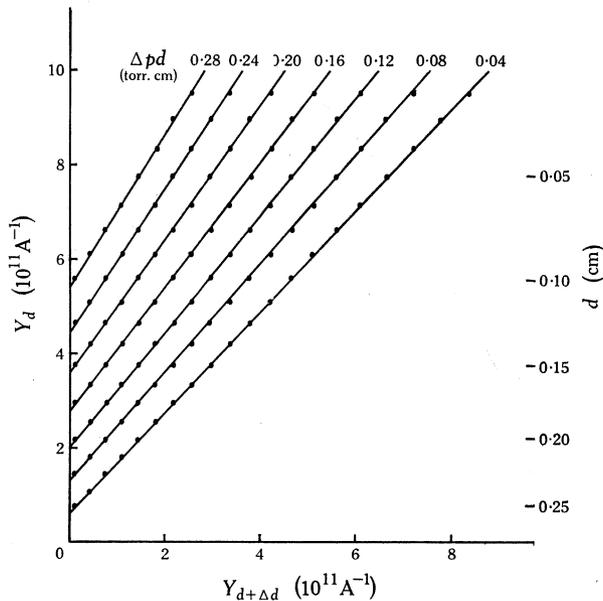


Fig. 2(b).—Family of Gosseries plots Y_d versus $Y_{d+\Delta d}$ for $E/p = 800$ $\text{V cm}^{-1} \text{ torr}^{-1}$ ($p = 1.61$ torr) using a gold film cathode and a solid anode. The effective value of a/p (from slope $\exp a\Delta d$ of linear portion) is 1.85.

it seems clear that much of the curvature must be attributed to the effects of non-uniform electric fields at low gap separations. It should be stressed, however, that, although the linearity of the plots leads to greater self-consistency in the analysis of results, it does not necessarily imply equilibrium conditions in the sense of a swarm concept and certainly does not imply that high accuracy can now be achieved in the evaluation of an effective value for a/p from the slope $\exp a\Delta d$ of the linear plots.

In fact, in the present experiments, the accuracy of the determinations decreases considerably with increasing E/p , but despite this it has not been possible at any stage to obtain values as high as those quoted by Rose and others at $E/p = 350$. Preliminary measurements have been made over an extended range of values of E/p and within the limits and assumptions imposed by the use of equation (2) the

variation of α/p is shown in Figure 3. Comparison with earlier plots of α/p versus E/p (von Engel 1965) shows that the peak in α/p is occurring at a very much lower value of E/p than previously anticipated. This is also true for other gases, although we have not as yet completed detailed investigations for gases other than hydrogen.

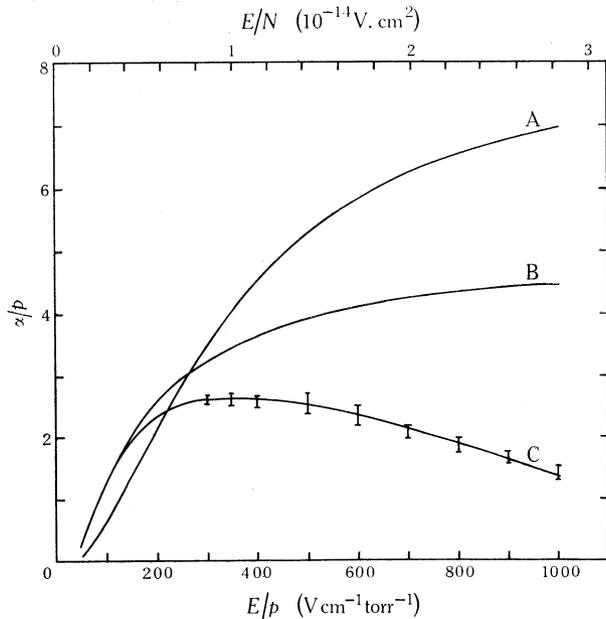


Fig. 3.—Values of α/p versus E/p (at 0°C); A, von Engel (1965); B, Rose (1956); C, present results.

VI. CONCLUSIONS

If, as seems to be the case, the upward curvature in the Gosseries plot must be associated with non-uniformity of the electric field, then the genuine non-equilibrium effects must be associated with the downward curvature displayed, for instance, in plots at $E/p = 100$. In this region we need to know how the primary coefficient α varies with distance d . If at large values of E/p there is a non-equilibrium situation for all values of d , then it is necessary to know also the detailed variation of the secondary coefficient with electrode separation. These variations, if any, are not known and are difficult to obtain either experimentally or theoretically.

In the absence of this information, analysis of the I, d measurements has in all recent investigations been carried out using equation (2). The present investigation has confirmed that in uniform electric field conditions the value of the primary ionization coefficient so obtained is very much lower than those quoted recently by Chanin and Rork and by Golden, Nakano, and Fisher. For example, at $E/p = 350$ we obtain $\alpha/p \simeq 2.6$, whereas the other research workers obtain values $\simeq 3.5$. These high values of α/p are obtained when measurements of current at low d , applicable to non-uniform fields, are included in the analytical procedure, and we conclude therefore that the high values previously reported are incorrect.

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