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Volume Recombination, Constriction, and Volt-Ampere Characteristics of the Positive Column

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Positive characteristics have been found for diffuse, striation-free, 1–20 ma dc, positive columns in 150-mm Xe, Kr, or Ar, with 0.1% N_2 in 10-cm tubes. With Xe+N_2, a continuous spectrum is emitted; with other rare gases selections of N_2 bands. The positiveness of the characteristic results from (1) the disappearance of ions principally by dissociative recombination and (2) ionization which is in effect single stage. For similar current densities the gradient varies little with tube diameter. Probe measurements indicate that the electron and ion density has a relatively flat distribution over a large central part of the tube as compared with the Bessel distribution; the latter resulting from ion loss to the walls by ambipolar diffusion. This broadening out of the discharge increases with the current. For steady convection-free discharges where volume recombination and diffusion are both contributing to ion loss, the degree of constriction should be governed by a "constriction number" C given by $C=D_a/\alpha R^2 n_e$, where D_a is the ambipolar diffusion constant, α is the recombination coefficient (supposed constant everywhere), R is the tube radius, and n_e the ion concentration.

When the current is increased beyond a critical value, the discharge changes abruptly to a filamentary form, the same whether N_2 is present or not, having a several-fold lower gradient, a negative characteristic, and emitting mainly the line spectrum of the rare gas. This discharge is believed to be diffusion and convection controlled, the (atomic) ions diffusing from the hot core to the cooler periphery where they form molecular ions and recombine dissociatively.

Such a mechanism as the above, involving a temperature gradient favoring the existence of molecular ions and dissociative recombination in the outer regions is believed to account quite generally for constriction greater than that corresponding to the Fabrikant-Spenke curve.

I. INTRODUCTION

As is well known, most positive columns have volt-ampere characteristics which are moderately to strongly negative. It is the purpose of this paper to describe a positive column which has a distinctly positive characteristic and to account for this positiveness as being due to important volume recombination.[1] A further purpose is to show the importance of volume recombination in helping to control the diffuseness (or constriction as the case may be) of steady convection-free positive columns.[2,3]

In most studies of the positive column at moderate to low gas pressures, volume recombination has been rightly assumed to be negligible. However, several authors have considered the possible effects of volume recombination and have shown that if the recombination coefficient α were constant everywhere, such recombination would tend to broaden the discharge[4] and would also tend to give it a positive characteristic.[5] It is well known that the positive column generally constricts with increasing gas pressure. Theories of this constriction have been reviewed by Fowler who has himself advanced a collision damping theory of the effect.[6]

Most positive column studies have concerned discharges at lower pressures where ion loss by diffusion to the walls was all important, or, as in convection stabilized or wall stabilized arcs at higher pressures, where volume recombination was all important. Particularly revealing has been a study of intermediate cases where both loss processes are important.

II. THE DIFFUSE DISCHARGE IN Xe+N_2

A typical intermediate-type discharge is one of a few ma dc and running in 120 mm pure Xe +0.1 mm N_2 in

[1] C. Kenty, Bull. Am. Phys. Soc. **6**, 385 (1961).
[2] C. Kenty, Report on the 21st Annual Massachusetts Institute of Technology Conference on Physical Electronics March, 1961 (unpublished), p. 172.
[3] C. Kenty, Proceedings of the 5th International Conference on Ionization Phenomena in Gases, Munich, August 28–September 1, 1961 (North-Holland Publishing Company, Amsterdam, 1962), Vol. I, p. 356.

[4] V. Fabrikant, Compt. rend. acad. sci. U.R.S.S. **24**, 531 (1939); R. Seeliger, Z. Naturforsch. **8a**, 74 (1953).
[5] A. Lompe and R. Seeliger, Ann. Physik **15**, 300 (1932).
[6] R. G. Fowler, Proc. Phys. Soc. (London) **68**, 130 (1955).

a 10-cm diam tube. A hot cathode is generally used. The positive column is diffuse, substantially filling the tube and emitting the white continuous spectrum of Xe only.[7] Convection currents are negligible. Probe measurements and measurements with a movable anode show that the column gradient is uniform along the tube. As the current is increased from 1 ma to 10 ma the gradient nearly doubles (Fig. 1), i.e., from 8.5 to 15 v/cm; at the same time the discharge broadens out, filling rather completely the tube. This broadening effect is evidenced by movable probe measurements of the electron (and/ion) concentration n_e (Fig. 2).

This diffuse discharge is believed to be running by two-stage ionization involving long-lived N_2 metastables, probably[8] $^3\Delta_u$. The ions are therefore probably N_2^+ and[9] N_4^+. Rough calculations of n_e based on electron mobilities in Xe, the measured gradient, and current density yield a value of $\sim 10^9$ cm^{-3} for the 10-ma case. Using reported[10] values for the dissociative recombination coefficient of N_2^+ [1.4×10^{-6} (ions/cc)$^{-1}$ (sec)$^{-1}$] and estimating the ambipolar diffusion coefficient (D_a) as ~ 1.5 cm^2 sec^{-1} it is calculated that the ion loss will be mostly by recombination except near the wall.

That the principal ion loss is by volume recombination is also indicated by the experimental result that, for similar current densities, the gradients are nearly independent of tube diameter. This may be seen from Table I, which shows gradients in an $Ar+N_2$ tube having two sections of different diameters. It is seen that at the higher current densities the gradients differ by only a few percent, whereas for many diffusion-controlled positive columns the gradient varies roughly inversely as the diameter for similar current densities.

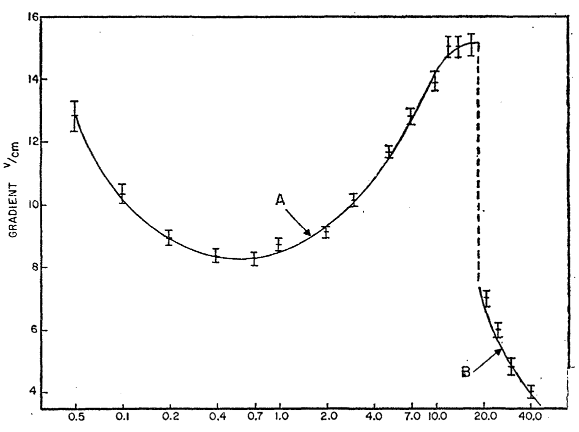

FIG. 1. A: Gradient-current characteristic for diffuse discharge. B: Characteristic for filamentary discharge. Tube is 10 cm in diameter and contains 120 mm $Xe+0.15$ mm N_2. Gradients measured with movable anode.

Other evidence for important volume recombination in the diffuse discharge comes from the abnormally small radial gradient (E_r). For pure diffusion-controlled columns the average E_r is of the same order as the axial gradient (E_a). For the 10-ma discharge of Fig. 2 the average E_r as found by the floating probe method, is only ~ 0.5 v/cm or $\sim 1/20$ E_a. As the current is reduced however the average E_r increases until for the 1-ma discharge it is ~ 1.4 v/cm or $\sim 1/6$ E_a; this indicates that ambipolar diffusion is becoming more important at the lower currents.

Experiments reported elsewhere[8] indicate that owing to the $\sim$1-sec life of $N_2(^3\Delta_u)$, the population of this metastable builds up to 10^{12}–10^{13} cm^{-3}. It is believed that this represents an essentially equilibrium population where production and quenching[11] of metastables by electrons are proceeding at equal rates. Under these circumstances the rate of ionization will be proportional to the first power of the current only. This being the case, preponderant loss of ions by volume recombination will easily be seen to account for the positive characteristic.

TABLE I. Axial gradients in 200 mm $Ar+0.14$ mm N_2 in a two-section tube as a function of current density. G_5: gradient in 5-cm diam section; G_{10}: gradient in 10-cm diam section. Gradients measured with movable anode.

I (ma/cm^2)	0.025	0.051	0.102	0.152	0.203	0.254	0.304
G_5 (v/cm)	27.4	29.4	32.0	33.2	34.0	34.6	35.3
G_{10} (v/cm)	21.8	25.4	29.8	31.9	32.8	33.5	34.2

If the current is lowered below 1 ma the volt-ampere characteristic flattens out and becomes negative; meanwhile contraction continues although the discharge remains diffuse. Probably now the N_2 metastable population is falling out of equilibrium with the electrons so that the ion production rate tends to decrease with n_e^2 while the diffusion loss, now relatively important, tends to fall off only with n_e. This means that a higher mean electron energy is required to maintain the needed ionization rate and hence a higher gradient is required. The effect is compounded to some extent because a higher T_e causes a still higher diffusion loss.

III. THE CONTINUOUS SPECTRUM

The diffuse discharge has an afterglow of a few seconds emitting the same continuous spectrum as the discharge. In the discharge the electrons besides exciting $N_2(^3\Delta_u)$ probably also excite Xe($^3P_2$, metastable). The energy of Xe($^3P_2$) is 8.28 ev and there is evidence that $N_2(^3\Delta_u)$ lies just below[8] 8.28 ev. This being so, one or two quanta of vibration, perhaps remaining unrelaxed from the discharge period or excited by gas kinetic collisions,

[7] Y. Tanaka and M. Zelikoff, J. Opt. Soc. Am. **44**, 254 (1954); C. Kenty, J. Chem. Phys. **22**, 1466 (1954).
[8] C. Kenty, J. Chem. Phys. **23**, 1555 (1955); **35**, 2267 (1961). For recent information on $N_2(^3\Delta_u)$ see P. G. Wilkinson, *ibid.* **32**, 754 (1960).
[9] M. Saporoschenko, Phys. Rev. **111**, 1550 (1958).
[10] S. C. Brown and W. P. Allis, *Basic Data of Plasma Physics* (Technology Press, Cambridge, Massachusetts, 1959), p. 195.
[11] R. W. Nicholls, J. Chem. Phys. **20**, 1040 (1952).

or by collisions of the slow electrons could enable $N_2(^3\Delta_u)$ to produce[8] $Xe(^3P_2)$ and so account for the afterglow as indicated below. The excitation of $N_2(^3\Delta_u)$ may be either direct or two-stage via the metastable $N_2(^3\Sigma_u^+)$ lying at 6.17 ev. Higher states of N_2 and Xe will probably not be directly excited because $Xe(^3P_2)$ will put an upper limit on the electron energies. Higher N_2 states if excited stepwise via $N_2(^3\Sigma_u^+)$ will be quickly quenched by Xe. Since no Xe lines are observed, $Xe(^3P_2)$ evidently attaches itself quickly to a normal Xe atom, probably with the help of a third body (Xe atom), to form Xe_2' and this excited Xe molecule radiates down to a repulsive state thus emitting the continuous spectrum.[8] This evidently happens before $Xe(^3P_2)$ can be further excited by an electron to emit the visible Xe lines; it is inferred also that it happens before $Xe(^3P_2)$ or Xe_2' can be ionized by electron collision. Therefore it is supposed as above noted that the ions are all N_2^+ and N_4^+.

IV. THE DIFFUSE DISCHARGE IN OTHER RARE GASES

Diffuse positive columns with positive characteristics have also been found with the other rare gases plus N_2. However with Kr+N_2 the glow and afterglow emit mainly a selection of the first positive bands of N_2. Here the lower metastable level of Kr, ($^3P_2$) lies too high (at 9.86 ev) to be excited in the presence of 0.1 mm N_2 (at considerably lower pressures of N_2 however the Kr continuum begins to appear). In Ar+N_2 the glow and afterglow consist of selections[8] of the first and second positive N_2 bands.

V. DIFFUSE DISCHARGES IN THE PURE RARE GASES

The pure rare gases at pressures of the order of 100 mm or more all have diffuse positive columns emitting continuous spectra only. In the case of Xe the spectrum is the same as if N_2 were present. The voltages are several to many times higher than if N_2 is present.[12] While these discharges have over-all positive characteristics, the positiveness appears to originate mainly in an extended region adjoining the hot cathode. The gradient increases steadily with distance away from the cathode but at a decreasing rate. At some 10 tube diameters away from the cathode the gradient reaches a substantially constant value and then appears to have a slightly positive characteristic. Determinations become difficult however as the tubes become quite long and the voltages high (5000–10 000 v). Further, only relatively small currents (1–2 ma) can be used or else the discharge will go over to a filamentary form which will now be described. The distribution of potential in the diffuse discharges in the pure rare gases is not understood, but is under further study.

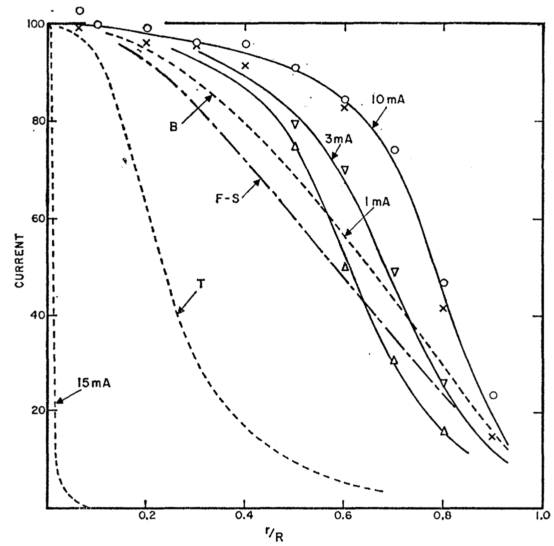

FIG. 2. Solid curves show relative distribution of n_e in diffuse discharge of Fig. 1 as a function of r/R, for 10 ma, 3 ma, and 1 ma. The points × and ○ for the 10-ma case are for two different runs. The upper point for the other curves are omitted to avoid confusion. n_e is taken to be proportional to the current collected by a movable probe at −40 v with respect to floating potential. These currents at the axis are 19.3×10^{-8}, 7.0×10^{-8}, and 3.1×10^{-8} amp, respectively, for the 10-ma, 3-ma, and 1-ma cases. The probe is a steel sphere 4.8 mm in diam and has a small quartz insulating sleeve. Curves B and F-S are the Bessel and Fabrikant-Spenke distributions, respectively. The curve marked 15 ma is schematic for the filamentary discharge of Fig. 1 and curve T is schematic for an intermediate case where dissociative recombination is important in the outer regions but not in the central ones.

VI. THE FILAMENTARY DISCHARGE

In any of the diffuse discharges so far mentioned, if the current is increased beyond a certain limit (5-fold higher if N_2 is present) the discharge suddenly goes into a filamentary form.[1,13] This discharge has a diameter of about 1 mm in Xe (somewhat larger the lighter the rare gas) and hence has a current density some 5000 times that of the diffuse discharge; it has a gradient one-third to one-half as great and has a negative characteristic and is convection controlled. It emits mainly the line spectrum of the rare gas plus a weak continuum just as if N_2 were present; in fact a little N_2 seems not to affect these filamentary discharges in any way. Presumably it runs by two-stage ionization of metastable rare-gas atoms. These metastables are also being further excited to give the visible rare-gas lines. At the relatively great current densities now prevailing such two-stage processes are more than able to compete with the process of molecule formation. By running the tube horizontally and deflecting the arc to the axis position with a known magnetic field it is possible to measure[14] the buoyant force and

[12] C. Kenty, Report on the 16th Annual Massachusetts Institute of Technology Conference on Physical Electronics, March 22–24, 1956 (unpublished), p. 80.

[13] G. Frind [Z. angew. Phys. 12, 515 (1960)], has studied constriction at higher currents in electronegative gases.

[14] C. Kenty, J. Appl. Phys. 9, 53 (1938).

hence estimate the arc temperature; this amounts to ~5000°K in 120 mm Xe. Such a temperature is not high enough for thermal ionization yet doubtless amply high to prevent the existence of rare-gas molecules and molecular ions. Such molecular species would also tend to be quickly dissociated by the strong electron bombardment prevailing. While some two-electron recombination[15] may be going on, it seems likely that most of the ions are reaching the convection-cooled periphery by ambipolar diffusion and there forming molecular ions and recombining.[16] Movable probe measurements show practically no conductivity from the wall up to within a few millimeters of the discharge.

In general the lighter the rare gas the higher the pressure required in order to obtain the filamentary discharge, e.g., in He~4 atm.

VII. GENERAL THEORY OF CONSTRICTION

The broadening of the diffuse discharge with increasing current above noted suggests that n_e at the axis is being held down by recombination; it also suggests that for steady discharges operated in the current range where volume recombination and diffusion losses are comparable, the degree of constriction (or diffuseness as the case may be) ought to be governed by a "constriction number" C expressing the ratio of the two losses. Thus the diffusion loss will be proportional to $2\pi RD_an_e/R$, where R is the tube radius and the recombination loss to $\pi R^2\alpha n_e^2$ and the ratio C will be given by

$$C = D_a/\alpha R^2 n_e.$$

Here it is supposed that α is constant across the tube. This constriction number is such that if α is negligible, C will be infinite and n_e will conform to the Bessell distribution, or in the case of two-stage ionization to the Fabrikant-Spenke distribution. On the other hand if D_a is negligible, C will be zero and n_e will be uniform across the tube.

For the 10-ma diffuse discharge in 120 mm Xe +0.1 mm N_2 in a 10-cm tube above described, C is estimated to be ~0.004. For a 0.4-amp discharge in a 3.6-cm i.d. tube containing 3 mm Ar plus 0.006 mm Hg (essentially the fluorescent lamp discharge which has approximately a Bessel distribution of n_e), C was calculated to be 4, based on $\alpha = 10^{-10}$, implying negligible volume recombination.

On the present view a degree of constriction greater than that corresponding to a Fabrikant-Spenke curve, can only occur when, relatively to the center, there is important volume recombination in the outer regions, i.e., when α increases to important values with increasing r. The above filamentary discharge is an extreme case; but it is probable that such a variation of α is very common, because of temperature increase toward the axis.

VIII. ACKNOWLEDGMENTS

The writer is indebted to Professor W. P. Allis, Miss M. A. Easley, Dr. B. T. Barnes, Dr. J. E. White, Dr. M. A. Weinstein, and Professor K. G. Emeléus for helpful suggestions.

[15] V. Fabrikant, see reference 4; N. D'Angelo, Phys. Rev. **121**, 505 (1961); D. R. Bates and A. E. Kingston, Nature **189**, 652 (1961) and other recent writers.

[16] K. G. Emeléus (private communication) has concluded that negative ion–positive ion recombination has an important bearing on constriction in discharges in electronegative gases.