Ion Concentrations and Recombination in Expanding Low Pressure Sparks*

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Passage of a capacitor discharge through a low pressure gas between electrodes results in an abrupt expansion of the gas along any avenues open to it. In hydrogen, the expanding luminous gas shows strong Stark broadening. Applying this effect, ion concentrations have been measured ranging up to 30 percent of the initial particle concentration. Intensity measurements indicate that the quantized radiation is a result of electronic recombination. Time and space studies show that the ion concentration appears to reach a maximum at some remote position down the expansion avenue, but that all discharges reach a maximum at about the same time.

I. INTRODUCTION

IT has been noted previously[1] that the luminosity fronts which move down expansion tubes during and subsequent to the discharge of a condenser through a confined gas at low pressure are accompanied by intense continua and a broadening of the spectral lines emitted, especially in hydrogen. Other workers have observed similar broadening in related situations. Finkelnburg,[2] using spark discharges in hydrogen at pressures of one atmosphere and above, noted strong broadening of the Balmer lines and an intense continuum, which he stated to be of different origin from the molecular continuum, and which he called the pressure continuum. He assumed the broadening to be Stark broadening, and calculated ion concentrations from them based on Holtsmark's[3] theory. Craggs and Hopwood[4] have utilized similar effects in their study of the expansion of initial spark streamers into full fledged arc columns during the course of a spark discharge. They point out that the contours of the broadened lines are just what would be expected of Stark broadening, and cite reasons for believing that the luminosity produced during the spark must be largely contributed by electronic recombination. We have observed these peculiar line contours in our discharges and arrived at the same conclusion: that they constitute the strongest evidence for interpreting the broadening as Stark broadening.

II. APPARATUS

The discharges under study were produced in the stem of a T-shaped quartz tube when a 15 μfd capacitor charged to potentials in the range from 3000 to 5000 volts was discharged between electrodes at the ends of the cross arm. The spectroscopic studies on the discharge were carried out with a Hilger E-1 quartz spectrograph. In ion concentration studies the tube was imaged on the slit of the spectrograph, so that a point by point record of the tube's luminosity could be obtained. In radiation law studies, the tube was placed close to the slit of the spectrograph so that light from a limited area of the tube (about 1 cm^2) filled the collimator. Photometry of the spectral lines was carried out on a Knorr-Albers microphotometer.

Accurate plate calibration with a discharge of the brevity of this one posed a problem of some difficulty. Our solution was to compare a series of spectra taken with multiple discharges of the tube on the assumption that reciprocity law failure was small, and that any intermittency effect was eliminated by the intercomparison of the data. This assumption is countenanced in some degree by Mees[5] and by information supplied by the Eastman Company[6] on its materials. It was further borne out by the agreement between data taken at different levels of intensity.

Pure hydrogen was obtained by diffusion through palladium.

III. EXPERIMENTAL RESULTS

1. Ion Concentrations

Half-widths of the broadened Balmer lines H_α, H_β, H_γ, and H_δ were measured as a function of position along the expansion tube for several gas pressures and several capacitor potentials. Each value is the average of three to five measurements at as many levels of exposure. The over-all agreement between half-widths measured at different exposures was quite good, the deviation from the mean being 13 percent.

2. Integrated Intensities

At two selected positions along the discharge tube, total integrated exposures and half-widths were measured simultaneously using the H_β line. Two methods of obtaining the integrated exposures were used with equal success. First, after study of several representative line contours had shown them to be of nearly Gaussian profile, the product of the maximum exposure and half-width for each line was used as a measure of the

* Research supported by the ONR.
[1] Fowler, Goldstein, and Clotfelter, Phys. Rev. **82**, 879 (1951).
[2] W. Finkelnburg, Z. Physik **70**, 375 (1931).
[3] J. Holtsmark, Physik. Z. **20**, 162 (1919); J. Holtsmark, Physik. Z. **25**, 73 (1924).
[4] J. D. Craggs and W. Hopwood, Proc. Phys. Soc. (London) **59**, 755 (1947).
[5] C. E. K. Mees, *Theory of the Photographic Process* (The MacMillan Company, New York, 1942).
[6] Eastman Photographic Plates for Scientific and Technical Use, sixth edition.

integrated exposure. Second, a number of actual profiles were converted from blackening to exposure, point by point, and planimetered as a check on the first method. This second method would be the method of choice were it not for the enormous amount of computation needed.

3. Continuum Studies

There is an intense continuum associated with the Balmer series. A spectrum of the discharge is given in Fig. 1. The origin of this continuum has not been definitely established. Some authors have assigned it a molecular origin, while others[2] speak of it as a "pressure" continuum, although the implication that it is caused by pressure processes seems doubtful. Experiments were therefore conducted to establish additional facts about it.

An attempt was made to detect the existence of a similar continuum in the vicinity of the Paschen series. Inferior dispersion and the rapid fluctuation of sensitivity with wavelength for Eastman Z plates made it difficult to interpret the spectra obtained, but a continuum was definitely observed. Whether the distribution of intensities in this continuum was similar to that of the Balmer associated continuum is debatable. The impression given by subjective study of the plates and photometer tracings is that the Balmer associated continuum is more far-flung than the Paschen continuum, extending as it does from some point between the series members at around 5000A to a point well below 2000A.

To investigate the possible molecular origin of the continuum, water vapor was substituted for hydrogen gas in the discharge. Before each discharge the tube was carefully pumped out to remove any hydrogen which might have formed during the previous discharge. The spectrum of the Balmer associated continuum was identical in every detail with that obtained in pure hydrogen. A few additional lines caused by the oxygen atoms were present in the spectrum. The continuum cannot, therefore, be caused by molecular dissociation in H_2.

Contrast of the Balmer associated continuum with the molecular continuum obtained from a glow discharge shows a considerable difference in the distribution of intensities, and calls attention to two other features of distinction: the thousandfold disparity between the intensities of the two continua, and the multiline spectrum which accompanied the molecular continuum but not the Balmer associated continuum.

It seems certain that at least part of the Balmer associated continuum is caused by recombination processes. Unless, however, the random fields of the ions produce some sort of enhancement and Stark broadening of the continuous levels of the atom as well as of the discrete levels, it seems probable that there is some other process than recombination responsible for a large part of the continuum. Another fact which points to this conclusion is that continua are observed in about this same general region 5000–3000A with all of the other gases which have been used, argon, neon, helium, and nitrogen. Hahn and Finkelnburg,[7] and Olsen and Huxford[8] have suggested that a bremsstrahlung process may be needed to explain this.

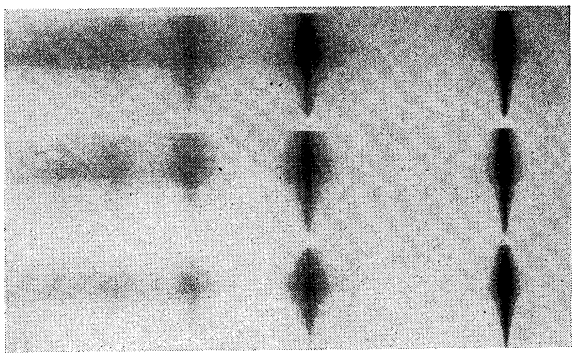

FIG. 1. Stigmatic spectrum of H_2 covering 14 cm of expansion chamber.

4. Level of Excitation

Spectrograms of the discharge in H_2 at pressures less than 1 mm show the tube wall is decomposed during the discharge. The spectra of these wall impurities have shown that excited systems having energies 167 ev above the ground state are present 5 cm down the expansion chamber. Silicon IV lines were graded in intensity, the lines being most intense at the head of the expansion chamber and becoming unobservable 5 cm down the expansion chamber. Silicon III lines had a slight intensity gradation and were visible 8 cm down the expansion chamber. Silicon II lines were visible throughout the entire 14-cm region investigated and had a maximum intensity 6 cm down the side tube. The lines of Silicon I were not present at all near the head of the expansion chamber, but were found throughout the lower 9 cm of the 14-cm region investigated. The ionized forms of oxygen showed analogous behavior.

Two alternative implications of the observed intensity distribution may be obtained. Assuming that the atoms are ionized and excited at the position where their spectra are observed, one would conclude that the energy available for ionizations decreased with distance down the expansion chamber. On the other hand, assuming that the atoms are all ionized in the main discharge tube and that they then travel to the point where their spectra are observed, one would conclude that a Si atom starts its journey as Si IV and captures electrons as it moves down the tube, becoming successively Si III, Si II, and finally Si I.

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[7] O. Th. Hahn and W. Finkelnburg, Z. Physik **122**, 37 (1944).
[8] H. N. Olsen and W. T. Huxford, J. SMPTE **55**, 289 (1950).

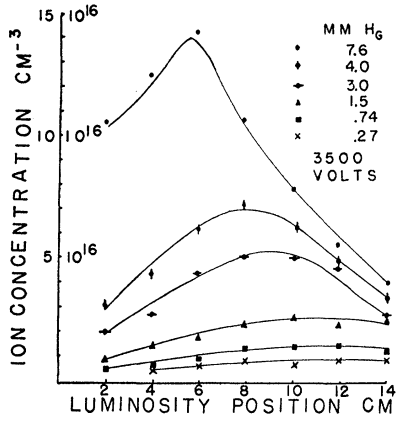

FIG. 2. Ion concentrations at constant voltage.

IV. INTERPRETATION

1. Ion Concentrations

The half-widths δ were interpreted as a measure of ion concentration n according to the relation of Holtsmark

$$\delta = 3.25 A e n^{\frac{2}{3}}.$$

Data computed in this fashion are given in Figs. 2 and 3. These data are weighted averages of the results from all four of the Balmer lines. In the application of Holtsmark's theory, estimation of the Stark coefficient A is a critical matter. Holtsmark defined it as the separation in cm^{-1} per unit field between the extreme Stark components of the line in question. He further assumed a uniform distribution of energy between the outermost components. As he was aware, and as Fig. 4 shows, this is not the case in actuality. Ion concentrations calculated on these assumptions do not show very close agreement between the results reported by different lines of the Balmer series. Considerable improvement can be made by replacing the separation between extreme Stark components by the separation between the widest pair which is strong enough to contribute significantly to the line intensity. In some cases, the extreme component is so weak that it has never as yet been detected experimentally.

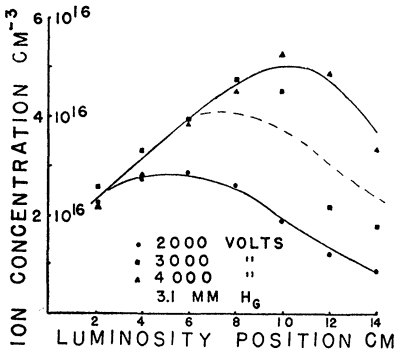

FIG. 3. Ion concentration at constant pressure.

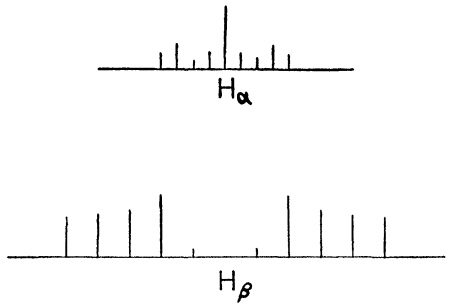

FIG. 4. Stark components of the Balmer lines.

While this change brings the two Holtsmark assumptions into better accord, there is still one feature of the component array which is completely neglected by the Holtsmark theory. The odd members of the Balmer series have a strong undeviated component which the even members lack. This results in a sharp peaking of the H_α and H_γ lines in comparison to the H_β and H_δ lines. A microphotometer tracing which shows this effect is given in Fig. 5. This characteristic serves as an identifying criterion for Stark broadening, but makes the calculations of ion concentration from the odd series members too low.

We have observed another effect which we believe also originates in the Stark effect, which will tend, on the other hand, to make the results from the even members too high. In the presence of extremely high fields, the H_β line is observed to be doubled. This is not ordinary self reversal because it is not shown by the other members of the series. It seems probable that it comes about because of the great vacancy in the center of the array of the even components. Holtsmark's distribution function for random fields has a maximum probability at a finite value of field intensity, and a zero probability of zero field. These two causes may combine to produce the splitting of H_β in strong random fields. The Holtsmark relation suggests another simple test for Stark broadening. The ratios of the half-widths of the various Balmer series members under any given condition are independent of ion concentration and strictly proportional to the ratios of the separations of the outer Stark components selected as discussed above.

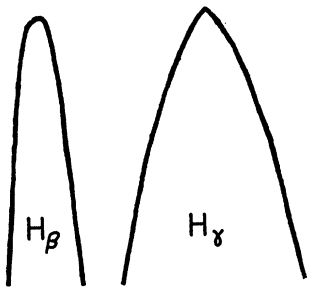

FIG. 5. Contours of H_β and H_γ.

These ratios are given in Table I. The agreement is best between lines of similar contour. The material of which the tube wall is composed has a considerable effect on the ion concentration observed. Higher concentrations are present in quartz tubes than in Pyrex. This fact is inferred from the extinction of the Balmer series at lower values of n in the latter case, although no measurements have been made as yet on line broadening. In Pyrex, the Balmer series terminates at H_θ, in quartz at H_ϵ. Rausch von Traubenberg[9] has shown that the complete washing out of the upper quantized states of an atom is a measure of the Stark fields in which the atom is placed. This approach can be used to obtain an independent estimate of the ion concentration, but has been neglected here in favor of the line broadening technique.

A special treatment of the ion concentration data reveals a regularity in the discharge which has not yet been explained. If the abscissas (positions along the expansion chamber) are divided by the initial velocity of the fronts to obtain a time, which we call a "synthetic" time, and the ordinates are divided by the product of gas pressure and capacitor potential, the data at all capacitances and gas pressures can be represented on a single graph within the experimental error. This graph is given in Fig. 6.

TABLE I. Internal consistency of half-widths.

Lines	Experimental average ratios	Theoretical ratios
H_γ/H_β	1.3	1.8
H_δ/H_β	2.7	2.8
H_δ/H_γ	2.2	1.6

2. Radiation Law

An investigation was next made of the relation between ion concentration as determined above, and the total integrated intensity of the H_β line. A logarithmic plot of these intensities against half-widths interpreted as concentrations is given in Fig. 7.

In actual fact, the quantity measured was not intensity, but exposure. Since the fronts at various pressures (and hence at different ion concentrations) pass the spectrograph's field of view in different time intervals because of their differing speeds, one would expect that a velocity correction should be made on these exposures to give a quantity more nearly proportional to the intensity. To make this correction the exposures should all be multiplied by the velocities of advance of the luminosities.

Another possible correction on the data is suggested by the mirrorgrams from which the front velocities were obtained. Each mirrorgram is a space-time diagram for the luminous gas, and duration of the luminosity at any point of the tube can be found directly from it. The duration of luminosity could be regarded as a measure of exposure time, and this correction might also be made.

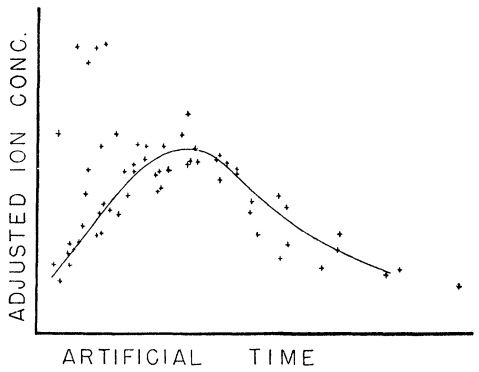

FIG. 6. Ion concentration *versus* time.

Neither of these corrections has been made on the data of Fig. 7. To make such corrections results in a much greater scatter of the experimental points, and introduces systematic differences between the points obtained with different capacitors. (We interpret this result as an indication that many of the radiating systems are not advancing with the front velocity. At first it was thought that perhaps all the radiating systems were at rest with respect to the tube, but Doppler measurements have shown that part of them at least are in motion with velocities which closely approximate the front velocity.) Whether or not the velocity corrections are made, the slope of the curve in Fig. 7 is very nearly two. Uncorrected it is 1.9. Corrected for velocity it is 1.8. Correction for duration reduces the slope to 1.5, but we do not feel that our present method of estimating these durations is adequate to rest any confidence in. Since the uncorrected data are always superior in agreement to the corrected data, it seems that in the final analysis it is possible that these corrections should not be made.

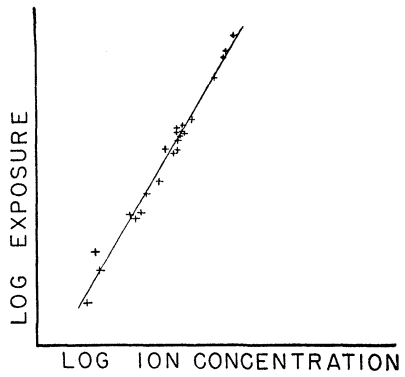

FIG. 7. Intensity *versus* ion concentration.

[9] H. Rausch von Traubenberg, Physik. Z. **31**, 958 (1930).

V. CONCLUSIONS

The expansion of a spark discharge is accompanied by moving luminosity in a highly ionized gas which appears to increase in ion concentration as the luminosity advances. The ion concentration can be estimated by analysis of the Stark broadening of the Balmer lines in hydrogen. The relation between radiated intensity and ion concentration for the moving luminosity is that which would be expected of random electronic recombination.

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Plural Electron Scattering and Its Influence on Electron Diffraction Patterns*

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The peak ring intensity (I_R') and the background intensity (I_B') for the most intense rings in the electron diffraction patterns of aluminium and thallium chloride have been measured, as a function of film thickness and accelerating voltage.

It is shown that part of the discrepancy between the results and the theories of Bethe and Morse is due to plural electron scattering.

A semi-empirical theory that includes the effect of plural scattering has been developed to explain the variation of I_R' and I_B' with specimen thickness. The contrast in the patterns (I_R'/I_B') increases rapidly with accelerating voltage and falls rapidly with increase in film thickness. The maximum film thickness (T_{max}) that will yield an observable pattern increases less rapidly than the accelerating voltage, between 50 and 150 kv, in agreement with the results of Möllenstedt.

INTRODUCTION

THE electron diffraction pattern obtained from a thin polycrystalline film of material consists of a number of rings seen against a continuous background. It has long been known that if the film thickness is increased, or the electron speed reduced, the intensity of the rings is reduced as compared with the background. In other words, the contrast in the pattern is reduced. Thomson[1] has attributed this to the attenuation of the diffracted beams by incoherent scattering in the film.

It has been difficult to treat this problem theoretically because of the complex character of electron scattering in the range of voltages and film thicknesses used. When electrons with energies of the order 10^5 electron volts pass through films with thicknesses between a few hundred and a few thousand Angstrom units (hereafter shown as A), they are, in general, scattered more than once, but not so many times that a mean angle of scattering can be calculated readily from a statistical consideration of the individual scattering processes. The phenomena is called plural scattering to distinguish it from multiple scattering in which the number of collisions is large enough to justify the use of statistical procedures. A general review of electron scattering has been given by Zworkin *et al.*,[2] who provide references to the earlier work.

The complexity of plural electron scattering also makes it difficult to interpret the results of scattering experiments. If the angular distribution of electrons scattered incoherently by a thin film is measured, there is no simple way of deducing the nature of the individual scattering processes from the results. On the other hand, the study of electron diffraction patterns permits the measurement of coherent and incoherent scattering in the same film and, hence, yields added information on the scattering process. As acknowledged below, the experimental realization of the method has been greatly facilitated by developments in other branches of experimental physics.

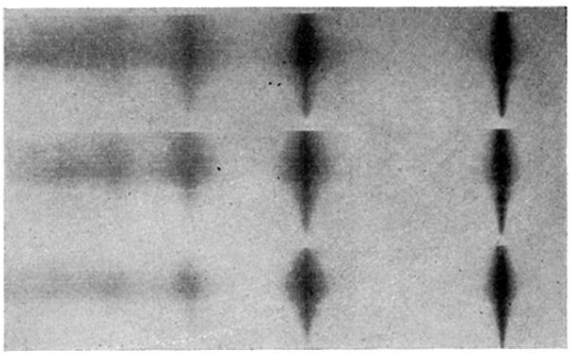
The electrons that enter the rings of a diffraction pattern must have been scattered in one of the following ways: (1) by an elastic coherent scattering process in one crystal; (2) by two or more elastic coherent scatterings in the same crystal. Such electrons have not made any incoherent or inelastic encounters. The electrons that enter the background have been scattered as follows: (3) by a single inelastic or incoherent scattering process; (4) by several successive encounters of type (3); (5) by a coherent scattering process of type (1) followed or preceded by scatterings of type (3) or (4); or (6) by successive elastic coherent scatterings in different crystals. In the type of pattern reported by Cowley, Rees, and Spink[3] such scatterings give rise to recognizable spots in the pattern. In the type of pattern discussed here, where the number of diffracting crystals is large, such spots would form part of the background; with many crystals none of the individual

* Part of this paper was presented at the National Bureau of Standards Symposium on Electron Physics, Washington, D. C., November 5–7, 1951.

[1] G. P. Thomson, Proc. Roy. Soc. (London) **A125**, 352 (1929).

[2] Zworykin, Morton, Ramberg, Hillier, and Vance, *Electron Optics and the Electron Microscope* (John Wiley and Sons, Inc., New York, 1945).

[3] Cowley, Rees, and Spink, Proc. Phys. Soc. (London) **A64**, 609 (1951).



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