

A SPECTROGRAPHIC EXAMINATION OF THE STRIATED DISCHARGE IN MIXED GASES*

BY DAVID A. KEYS AND M. S. HOME

ABSTRACT

The present paper contains the results of a spectroscopic examination of the striated discharge in (1) a mixture of nitrogen and hydrogen, (2) a mixture of helium and hydrogen. Spectrograms were taken of the light emitted by the negative glow and by the striations respectively. The electronic energies in the different regions of the discharge are interpreted from these spectra in much the same manner as that first suggested by Seeliger and now used by astrophysicists to determine the extent of ionization in different stars and in various levels of the sun's atmosphere from the spectra of their regions. In the nitrogen mixture the Balmer lines and the nitrogen bands 4708, 4278 and 4236 were found to appear in the negative glow but to be absent from the striations. Interpreting this result in terms of electronic energies (or equivalent quanta, if radiation) there are relatively few electrons possessing energy equivalent to 15.5 volts in the striations though the potential applied to the discharge tube was about 1100 volts. In the mixture of helium and hydrogen, the Balmer lines are strong in the striations but relatively weak in the negative glow. The line spectrum of helium was strong in the negative glow but weak or absent in the striations. The mercury arc lines were equally strong in both parts of the discharge. In terms of electronic energies, these results mean that there are relatively few electrons possessing energy equivalent to 25.3 volts in a striation but plenty possessing energies of 10.4 and 15.5 volts. An explanation is suggested of the change in intensity of certain lines in mixtures of different gases.

THE following experiments are a continuation of a former paper,¹ in which the spectra from the different regions of a striated discharge are examined with a view to determining (I) the relative concentration of the different atoms and molecules in the various excited states and (II) the distribution of potentials or electronic energy in the same regions. The distribution of potential and the electric field in different parts of a striated discharge have been measured by many investigators. The various methods which have been used may be classified under the following four groups: (A) the exploring electrode,² (B) the cathode ray beam,³ (C) the Stark effect,⁴ (D) the hot and cold sounding probe

* Read in abstract, Kansas City Meeting of the American Physical Society, December, 1925.

¹ D. A. Keys, *Trans. Roy. Soc. Canada* **19**, 143 (1925).

² J. J. Thomson, "Conduction of Electricity through Gases." 2nd Edition p. 528.

³ J. J. Thomson, *Phil. Mag.* **18**, 441 (1909); F. W. Aston, *Proc. Roy. Soc. A.*

⁴ E. Brose, *Ann. d. Physik* **58**, 731 (1919).

method due to Langmuir.⁵ The unreliability of A and the limitations of B and C are quite evident. The presence of the probe in those experiments in which the Langmuir method has been used, has been found not to distort the field appreciably. In these cases the current density has been comparatively large. But in discharges of small current densities such as are used in the present paper any obstruction in the path of the discharge is more liable to alter conditions. Moreover, under the conditions of the experiments to be described, the discontinuities in the current potential curves obtained by the Langmuir method would be very difficult to designate with accuracy. The method adopted in this paper was therefore similar to that used by Seeliger,⁶ who observed the variation in intensity of certain spectral lines in different regions of a glow discharge. The light emitted by different regions of the discharge was photographed with a spectrograph and from the nature of the spectra the potentials or electronic energy necessary to produce the lines determined.* The gas is thus made to reveal its own condition and the potentials are determined in much the same manner as that used by astrophysicists⁷ to determine the extent of ionization among the different atoms in the various stars and in the different depths of the stellar atmosphere of the same star, by examining the light which they emit or absorb. The method is limited by our knowledge of excitation and ionization potentials but some information may be obtained when these potentials are known. One of us has already pointed out some differences in the spectra from different parts of a single striation and the negative glow in the case of hydrogen.¹ The present paper contains the result obtained from the examination of (i) a mixture of nitrogen and hydrogen and (ii) a mixture of helium and hydrogen.

APPARATUS

The apparatus used was similar to that described in an earlier paper,¹ consisting of a glass tube about 95 cm long and 5.5 cm in diameter, fitted with parallel plane aluminium electrodes. The potential difference between the electrodes was about 1100 volts and the current about 10 milli-amps. supplied by an Evershed and Vignolles direct current generator. The spectrograms were taken with a Hilger constant de-

⁵ I. Langmuir, *J. Frankl. Inst.* **196**, 751 (1923).

⁶ R. Seeliger, *Ann. d. Physik* **67**, 352 (1922).

* It has been suggested to the authors that the Langmuir probe method might have been used to measure the velocity distribution and thus directly test the relation suggested. We hope to try this later.

⁷ Saha, *Proc. Roy. Soc.* **A99**, 136 (1924).

viation glass spectrograph. The tube was exhausted by a Hyvac oil pump and a charcoal tube cooled with liquid air. The gases were dried with phosphorus pentoxide and the discharge tube was washed out thoroughly several times with the gases before a photograph was taken, the discharge passing through each rinsing in order to remove as much as possible of the "residual" gases from the electrodes. No attempt was made to bake the tube or the electrodes.

OBSERVATIONS

Nitrogen and hydrogen. The nitrogen was prepared by heating a solution of potassium nitrite and ammonium chloride, the gas being purified by passing it over heated copper turnings to remove any trace of oxygen present and over phosphorus pentoxide to remove the water vapor. Some observations were first made on the relation between the current and the applied potential. It was found that at a certain potential the current rose rapidly without any change in potential, the pressure of the gas being about 0.01 cm of mercury. On

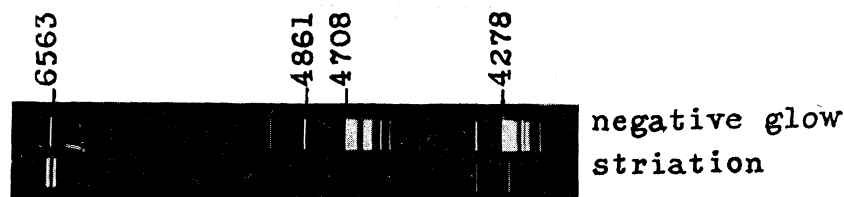


Fig. 1. Spectrogram of the striated discharge in a mixture of nitrogen and hydrogen.

reducing the potential the current did not fall to its former value, confirming Olsen and Young's observation,⁸ who attribute this fact to the charging up of the walls of the tube. The potential was then kept constant at about 1100 volts and spectrograms were taken of the light emitted by the negative glow and by a striation. The results are shown in Fig. 1. It will be seen that the lines $H\alpha$ and $H\beta$ come out strongly in the negative glow but are absent in the striation. To produce the Balmer lines from molecular hydrogen requires 15.5 volts and to produce the negative bands in nitrogen requires 17.75 volts.⁹ *It therefore appears that there are no electrons present in the striation possessing energy equal to 15.5 volts, though the potential between the ends of the tube is 1100 volts.* If we assume a Maxwellian distribution for the energy of electrons, the results show that the center of this

⁸ A. R. Olsen and T. F. Young, *Phys. Rev.* **25**, 58 (1925).

⁹ E. E. Witmer, *Phys. Rev.* **26**, 780 (1925).

distribution corresponds to an energy less than 15.5 volts in the striation.

Helium and hydrogen. Helium with a small trace of hydrogen was now used in the tube. Some interesting changes in the nature of the discharge were noticed during this washing. When the striations were first formed they were not equally spaced, the distance between the striae near the anode being only about one-half that between those near the cathode. A stria would appear to vanish in the middle of the positive column without any visible effect on its neighbors. The phenomenon lasted about a minute and was not observed in any subsequent work. This effect is attributed to nitrogen liberated by the electrodes. On commencing the discharge the striae were formed at once but were not clearly defined. After about ten minutes they became quite sharp but in an hour they commenced to degenerate into

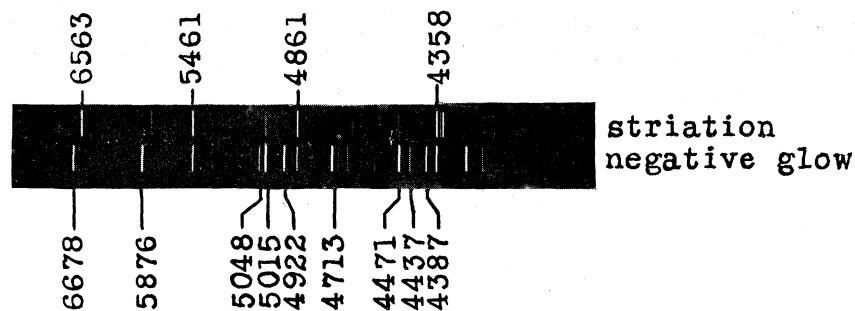


Fig. 2. Spectrogram of the striated discharge in a mixture of helium and hydrogen.

the continuous positive column and after two hours the column was continuous except for two striations near the cathode end. The current was then raised from 10 to 12 milli-amps. and in a few minutes the striae returned to their former sharpness. This was repeated several times during each washing. No visible change in pressure could be detected with the McLeod gauge during this degenerating process. All traces of nitrogen were finally removed and after leaving the tube connected for three hours with the charcoal tube cooled with liquid air, the discharge settled down to a steady state, a trace of mercury vapor and hydrogen being the only impurities present. A typical spectrum of the negative glow and of a striation is shown in Fig. 2. Table I gives some of the principal lines and their relative intensities measured in these photographs. The notation is that used by Fowler.¹⁰

¹⁰ A. Fowler, "Report on Series in Line Spectra."

The table shows that the line spectrum of helium is strong in the negative glow but it is practically absent in the striation, the only series which show any tendency to persist being the $1S-mP$ and $1\pi-m\delta$.

From these spectrograms we see that the helium lines are strong in the negative glow and very weak or absent in the striation. The hydrogen Balmer lines however are strong in the striation and weaker in the negative glow. This is just the reverse of what is the case when hydrogen alone is used.¹ The mercury lines 5461, 4358 and 4047 are

TABLE I

Lines in the spectra of the negative glow and of the striations. Helium and hydrogen mixture.

| Series type | Wave-length | Negative glow | Striation |
|----------------|-------------|---------------|---------------|
| $1S-2P$ | 5015 | Strong | Fairly strong |
| $1S-3P$ | 3965 | Weak | Absent |
| $1P-2D$ | 6678 | Strong | Very weak |
| $1P-3D$ | 4922 | Strong | Very weak |
| $1P-4D$ | 4387 | Strong | Very weak |
| $1P-5D$ | 4144 | Weak | Very weak |
| $1P-3S$ | 5048 | Strong | Absent |
| $1P-4S$ | 4437 | Strong | Absent |
| $1\pi-2\delta$ | 5876 | Strong | Weak |
| $1\pi-3\delta$ | 4471 | Strong | Weak |
| $1\pi-4\delta$ | 4026 | Strong | Absent |
| $1\pi-3\sigma$ | 4713 | Strong | Very weak |
| $1\pi-4\sigma$ | 4120 | Weak | Absent |
| $H\alpha$ | 6563 | Very weak | Strong |
| $H\beta$ | 4861 | Fairly strong | Strong |
| Hg | 5461 | Strong | Strong |
| | 4358 | Strong | Strong |
| | 4047 | Strong | Strong |

equally strong in both parts of the discharge. Interpreting these results in terms of electronic energies, we see that relatively few electrons have energy equivalent to 25.3 volts in the striation but that a large number have energy equivalent to 10.4 volts (to produce the mercury lines) and 15.5 volts to produce the Balmer lines.

In contrast to the behavior of hydrogen in nitrogen, the Balmer lines $H\alpha$ and $H\beta$ in the mixture of hydrogen and helium are much fainter in the negative glow than in the striation. Furthermore, the two lines in the latter case show a curious reversal of intensity in the negative glow. $H\alpha$ is very faint while $H\beta$ is much stronger though the normal intensity of $H\alpha$ is greater than that of $H\beta$. It appears that the presence of helium in some way prevents the excitation of these two Balmer lines in the negative glow and enhances them in the stria-

tions. Merton and Pilley¹¹ have shown that the presence of helium at high pressures increased the intensity of the N^+ lines in the positive column and McLennan and Shrum¹² found that the presence of helium or neon brought out the famous green line 5577 in oxygen. Now we have shown that the Balmer lines are affected in the same manner, and the same explanation may be applied to their experiments as to ours, namely that the inert gases cause a redistribution of the electronic energy so that the maximum energy occurs in a region which will excite these lines in all three cases just cited. Compton¹³ has given an explanation of Merton and Pilley's results as being due to optical excitation by collisions of the second kind. According to the theory of Klein and Rosseland, the probability of such excitation taking place decreases as the difference between the energy of the excited atom and that required to excite the second atom increases. The difference between the excitation potential of $H\alpha$ and $H\beta$ is very small, and, though the probability of $H\beta$ being optically excited by the excited or ionized helium in the negative glow is greater than that of $H\alpha$, the difference in this probability seems hardly sufficient to account for the result that $H\beta$ is so much stronger than $H\alpha$. Hughes and Klein¹⁴ have shown that the fraction of the collisions of electrons with atoms and molecules which result in *ionization* increases to a maximum and then decreases as the energy of the electrons increases. On the supposition that the $H\alpha$ and $H\beta$ lines are excited directly for the most part by electrons, this reversal of intensity of $H\alpha$ and $H\beta$ in the negative glow would mean that the Maxwellian distribution of energy among the electrons in the negative glow has a maximum which has a higher energy value than that required to excite the $H\alpha$ line. In a discharge tube using a hot cathode and a mixture of mercury vapor and hydrogen, Turner and Compton¹⁵ have shown that the arc spectrum of mercury is emitted both from the negative glow and from a striation, and Compton, Turner and McCurdy¹⁶ found no trace of the hydrogen lines in the striations in a similar experiment, while the Hg bands were found in the striations. This is a result similar to the behavior of hydrogen as found in our experiments. Work is being continued using still larger discharge tubes and different gaseous mixtures to see how the

¹¹ T. R. Merton and J. C. Pilley, Proc. Roy. Soc. **A107**, 411 (1925).

¹² J. C. McLennan and J. M. Shrum, Proc. Roy. Soc. **A 108**, 501 (1925).

¹³ K. T. Compton, Phil. Mag. **50**, 512 (1925).

¹⁴ A. L. Hughes and E. Klein, Phys. Rev. **23**, 450 (1925).

¹⁵ L. A. Turner and K. T. Compton, Phys. Rev. **25**, 606 (1925).

¹⁶ K. T. Compton, L. A. Turner and W. H. McCurdy, Phys. Rev. **24**, 597 (1924).

distribution is affected by the diameter of the tube, the different gases present and their relative concentrations.

CONCLUSION

1. Spectrograms have been taken of the negative glow and of a striation in mixtures of (i) nitrogen and hydrogen (ii) helium and hydrogen.

2. In the case of the nitrogen mixture, the Balmer lines $H\alpha$ and $H\beta$ and the nitrogen bands 4708 and 4278 appear in the negative glow, but are absent from the striation.

3. In a mixture of helium and a trace of hydrogen the helium line spectrum is strong in the negative glow but weak or absent in the striations. The hydrogen lines are strong in the striations but relatively weak in the negative glow. The mercury lines are strong in both parts of the discharge. $H\alpha$ is much weaker than $H\beta$ in the negative glow.

4. A method of interpreting the electronic energies in different parts of the discharge from the spectra emitted has been followed. On this hypothesis there are relatively few electrons possessing energy equivalent to 15.5 volts in the striations in the nitrogen mixture. Also in the case of the helium mixture, a relatively small number of electrons have energy equivalent to 25.3 volts, but there are plenty with energies equivalent to 10.4 and 15.5 volts in a striation.

5. An explanation of this change in the distribution of the intensity of certain lines in mixtures of gases is suggested on the supposition of a change in the position of the peak of the Maxwellian distribution of energy among the electrons.

THE MACDONALD PHYSICS BUILDING,
MCGILL UNIVERSITY,
February 15, 1926.

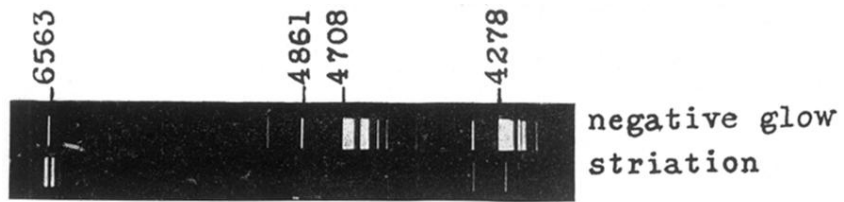


Fig. 1. Spectrogram of the striated discharge in a mixture of nitrogen and hydrogen.

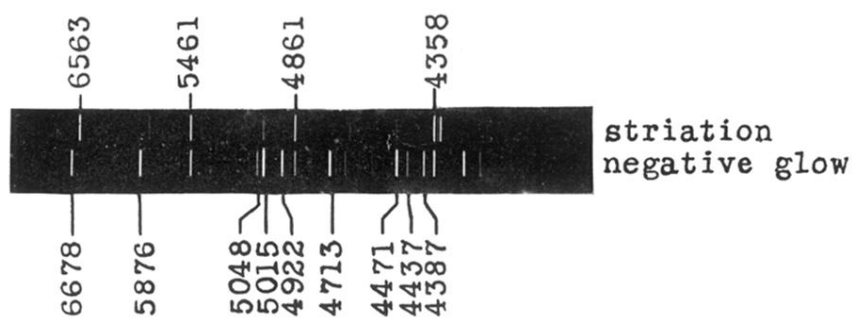


Fig. 2. Spectrogram of the striated discharge in a mixture of helium and hydrogen.