INTENSITIES IN THE HYDROGEN SPECTRUM.

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Abstract.

Variation of the intensity of hydrogen spectrum lines with the energy of the exciting electrons, 29 to 110 volts, pressure and current being maintained constant, was studied quantitatively by the use of a three-electrode tube in which electrons from a long oxide-coated filament were accelerated through a nearby grid with a field-free space between the grid and the plate. The spectra of light from this space, excited with various accelerating potentials, were photographed on the same plate and the densities of certain lines were measured by a microphotometer. Of the *series lines*, $H\alpha$ shows practically constant density for the whole range of voltage, while $H\beta$, $H\gamma$ and $H\delta$ increase in density at first rapidly and then more slowly, tending to constant values for the higher electron energies. The density change was greater the higher the term number. Of the *lines of the secondary spectrum*, λλ 6327, 6225, 6135, 6122, 6030 and 6018 decrease very rapidly in density as the energy of the electrons is increased, while λλ 5013, 4934, 4929, 4743, 4632 and 4205 reach maximum density between 30 and 40 volts and then grow weaker but not as fast as the first six lines. Since the series spectrum is associated with the atom and the secondary with the molecule, it is inferred that the *ratio of dissociating to non-dissociating collisions* increases rapidly with the energy of the bombarding electrons between 29 and 110 volts. The change in relative intensity of the series lines suggests that the higher the energy of electron impact the more likely is the electron within the atom to be displaced to the remoter Bohr orbits when the molecule is dissociated.

IT is a matter of common observation that the distribution of intensities in the spectrum of hydrogen varies enormously as the conditions of excitation are changed. Though it is evident that a study of the conditions causing intensity variations might well lead to information on the nature of the origin of the spectrum, quantitative studies of the intensities in the hydrogen spectrum are very few. Merton and Nicholson [1] give an account of some measurements on the changes in distribution of energy among the first four lines of the Balmer series when a condensed discharge is substituted for an uncondensed discharge. The independent variable, however, in this type of work is not a clearly defined quantity. It seemed, therefore, worth while to try and measure the intensities of the hydrogen lines as a function of some definite fundamental variable. The generally accepted theory of radiation is that radiation is given out when the atom (or molecule) has been put into an abnormal state by radiation, or by electron impacts, and is returning to its normal state. If we con-

[1] Phil. Trans. Roy. Soc., A, 217, p. 237, 1917.

fine ourselves to the case when the atom or molecule is radiating as a result of a collision with an electron, then clearly the energy of impact of the electron is the important fundamental quantity governing the emission of radiation. It is, of course, recognized that the resulting effect may be profoundly affected by other factors, *e.g.*, pressure which determines the proximity of the molecules. Nevertheless, it is the impact of the electron which puts the atom into a state in which it can emit radiation and one can imagine a state of affairs (very low pressure, very feeble currents) in which the subsequent factors controlling the radiation become negligible.

The method employed by Fulcher[1] was to accelerate electrons from a hot cathode by a definite potential to an anode. Spectrograms of the light excited by collisions in the intervening space were taken for different accelerating potentials. Fulcher found that, as the velocity of the electrons was decreased, the secondary spectrum (at least many lines belonging to it) was much intensified with respect to the Balmer series. Holtsmark[2] accelerated electrons from a hot cathode to an anode in which there was a suitable opening through which some of the electrons could pass into a space where there was no electric field. He measured the intensities of the four leading Balmer lines radiated from this space, and found that the ratios of the lines $H\alpha$, $H\beta$, $H\gamma$, and $H\delta$ were unchanged as the energies of the electrons were increased from 17 volts to 1,700 volts.

The secondary spectrum is very complicated. Merton and Barratt[3] give a list of over 1,000 lines, in which they indicate the manner in which many of these lines are affected by variations in conditions of excitation. Some lines are relatively intensified at high pressures, some at low pressures, some by a condensed discharge, and some in the presence of helium. Certain lines are designated as "Fulcher Lines," being those observed by Fulcher as intense lines when excited by low velocity electrons. Merton and Barratt were unable to arrive at any comprehensive generalization, but on the whole they found that those lines which were relatively intensified at low pressures were Fulcher lines, while lines which were relatively intensified at high pressures (and generally with a condensed discharge) were not Fulcher lines.

In the present investigation, the authors have measured the intensities of the first four Balmer lines and a number of the more prominent secondary lines. The authors were unaware of the work of Holtsmark until

[1] Astrophysical Jour., 37, p. 60, 1913.
[2] Phys. Zeits., 15, p. 605, 1914.
[3] Phil. Trans., A, *222*, p. 369, 1922.

after the investigation was completed; their results are not in agreement with those of Holtsmark.

Apparatus.

A V-shaped oxide-coated filament, about 20 cms. total length, served as the source of electrons. Parallel and close to the filament was a grid of fine nickel wire. Beyond the grid was a semicircular nickel plate approximately fitting the glass tube. The plate and grid were both connected to the positive end of the battery giving the accelerating voltage, while the other end was connected to the filament. The electrons were quickly accelerated to the grid and then passed into a field-free space with a velocity determined by the accelerating potential. A two-prism photographic spectrometer was lined up so that the axis of the collimator was along the axis of the field-free space between the plate and grid. Thus, we photographed the spectrum produced by the impact of electrons of definite velocity (the pressure being kept sufficiently low to ensure that only a small percentage of electrons made a second collision within the field-free space). Hydrogen was generated from pure zinc and sulphuric acid and passed through phosphorus pentoxide and through charcoal cooled by liquid air, into a reservoir. It was passed into the apparatus through a fine capillary glass tube, the pumps being in action continuously. In this way, a stream of hydrogen was passed through the apparatus, the pressure remaining very constant. U-tubes on the inlet and outlet sides of the experimental tube were cooled by liquid air.

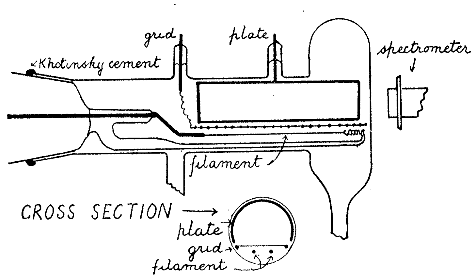

Fig. 1.

Panchromatic plates were used so as to photograph the whole spectrum. Many photographs were taken to find out the best conditions. The final plates, giving the results recorded in this paper, were taken under as constant conditions as possible. Ninety minutes' exposure was given for each spectrogram on the first two plates, the pressure and the current through the field-free space being kept constant. On the first plate exposures were made with 110, 85, 50 and 35 volts accelerating potential. On the second plate exposures were made with 110 volts (to link up with the first plate), 65, 40 and 34 volts. On the third plate there were two exposures of four hours each corresponding to 29 and 35 volts. The electron current for the first two plates was 50 milliamperes and the pressure was .050 mm. For the third plate the current was 5 milliamperes and the pressure .072 mm.

The "opacities" of the lines on the photographic plate were measured by a microphotometer.[1] The results are given in "densities," the relation between density D and opacity O being given by

$$D = \log_{10} O.$$

Unfortunately we had no means of calibrating our plates so as to deduce the intensity of the radiation in any line from the opacity of the line on the plate. However, it is well known [2] that the density is proportional to the logarithm of the exposure or, when the time of the exposure is unchanged, to the logarithm of the intensity, except when the density is very great or very small in which case a small change in density indicates a greater change in intensity than over the straight portion of the curve. So far as our measurements are concerned, only lines of small densities are likely to be affected in this sense. We have left our results in densities.

Results.

Fig. 2 gives the curves connecting the densities of the Balmer lines with the voltage accelerating the electrons.

As Fig. 2 shows, the values for 110 volts on both plates are (except for H_γ) practically identical, indicating that, so far as the 110-volt exposures go, the plates are fairly comparable. Unfortunately there is an appreciable difference in shapes of the curves for the two plates. However, the difference between them does not affect the conclusions drawn. The spectrograms obtained in the standard time, $1\frac{1}{2}$ hours, for voltages below 34 volts were so weak that it was necessary to give much longer exposures. Hence spectrograms for 29 and 35 volts were taken on plate 3, the exposures lasting 4 hours. As higher current could not be obtained at 29 volts, current was maintained in both cases at 5 milliamperes and to get more light the pressure was increased a little to .072 mm.

[1] We are indebted to Dr. Foote, of the Bureau of Standards, for the design of an improved form of microphotometer. The method of using it is sufficiently described in "A New Microphotometer," Bur. Stand., Sci. Papers, No. 385, 1920, by Drs. Meggers and Foote.

[2] See Davis and Walters, "Sensitometry of Photographic Plates," Bur. Standards, Sci. Papers, No. 439, 1922.

To link the 29-volt spectrogram on plate 3 with those on plate 1, we measured the difference between the densities of the lines for 35 volts in plate 1 and the corresponding densities in plate 3, and added this difference to the 29-volt densities in plate 3. This method may be open to criticism. Its validity implies that the density is proportional to the logarithm of the exposure. It would have been more satisfactory of course to get the 29-volt spectrogram under exactly the same conditions as the others, but this was not practicable.

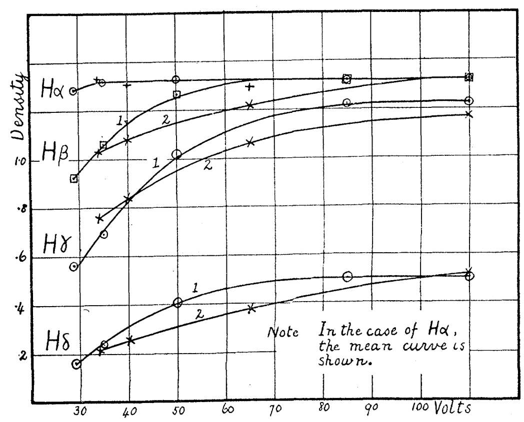

Fig. 2.

The Balmer Lines.—H_α remains practically unchanged in density from 30 to 110 volts. H_β, H_γ, and H_δ increase in density as the voltage increases and tend to reach a constant value as the voltage approaches 110 volts. Between 29 and 110 volts H_β changes in density by .41, H_γ changes by .62, while H_δ changes by only .34. It was mentioned earlier that when densities are *small*, a given change of density corresponds to a much larger change in the logarithm of the intensity than it does on the straight portion of the characteristic curve for the plate. Hence the density change for H_δ may, in reality, mean a greater relative change in its intensity as the voltage is increased from 29 to 110 volts than for H_γ. If this is the case, and it seems most probable from other data, we could generalize the results and say that, as the energy of impact decreases from 110 volts to 29 volts, the distribution of energy among the Balmer lines is at first practically constant and then alters more and more rapidly as the voltage is decreased. The alteration is such that the intensity of the H_α line remains almost unchanged over the whole range, while the intensities of the other lines decrease, the amount being greater, the higher the term number of the line.

The Secondary Spectrum.—In selecting twelve prominent secondary lines for measurement, we first of all tried to choose lines about which there could be no confusion as to identity on our plates and then, among

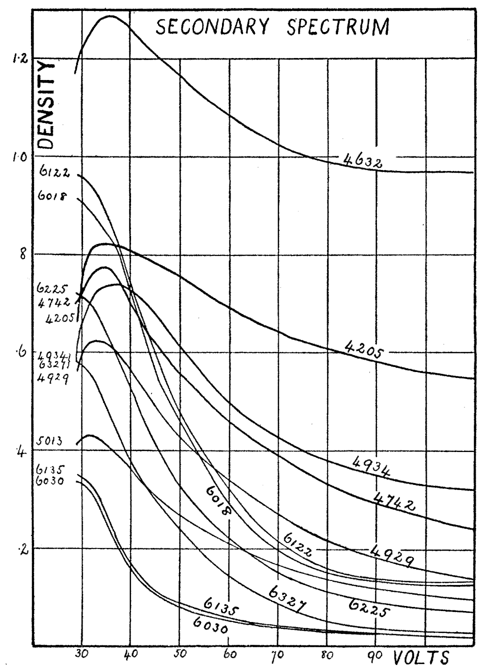

Fig. 3.

these, we chose lines which represented the various classes indicated by Merton and Barratt.[1]

To present the results for these secondary lines in the same way as for the Balmer lines would require twenty-four curves. To avoid unnecessary confusion, a mean curve was drawn for each line from the densities on the three plates and only such mean curves are shown. (The curves are of course not so smooth as the absence of marked points may imply.)

The curves fall into two classes. λ 6327, λ 6225, λ 6135, λ 6122, λ 6030 and λ 6018 have no maximum, and their intensities (as inferred from their densities) fall off exceedingly rapidly as the accelerating voltage is increased. (Earlier remarks on the interpretation of very small densities should be remembered if doubts arise as to the applicability of this statement to the weaker lines λ 6135 and λ 6030.) The lines in the other class, λ 5013, λ 4934, λ 4929, λ 4632, λ 4743, and λ 4205, have a maximum density between 30 and 40 volts, and their densities do not

[1] Loc. cit.

fall off so rapidly with increasing voltage. This division falls in fairly well with Merton and Barratt's classification.

Of the lines in our first class, λ 6327, λ 6225, λ 6122, and λ 6018 are classified by Merton and Barratt as "low pressure" lines and as Fulcher lines. λ 6030 may be a mixture of λ 6032 and λ 6028, the former being a "low pressure" and a Fulcher line. The remaining line λ 6135 seems to be an exception, for they record it merely as a "high pressure" line. However this must be a mistake for Fulcher records it as one of the main band lines.

In our second class, we have no lines which Merton and Barratt designate as Fulcher lines. Only one line, λ 4743, is a "low pressure" line. This is probably a fusion of λ 4743.4 and λ 4742.7, the former of which is classed as a "low pressure" line, while the latter is not characterized in any way. The other lines are apparently indifferent to pressure as Merton and Barratt do not list them either as high or low pressure lines. Three of them, λ 4934, λ 4929, and λ 4632, are noted as lines which show the Zeeman effect. (Apparently no Fulcher line shows the Zeeman effect).

Discussion.

The possible results of a collision between an electron and a hydrogen molecule are given in Table I.

Table I.

		Min. Energy Required.
No dissociation:	(1) Ionized molecule.	?
	(2) Partially ionized molecule [1].	?
Dissociation:	(3) Neutral atom and partially ionized atom.	3.5 + 10.2 = 13.7 volts.
	(4) Neutral atom and ionized atom.	3.5 + 13.5 = 17.0 volts.
	(5) Two partially ionized atoms. . . .	3.5 + 2 × 10.2 = 23.4 volts.
	(6) Ionized atom and partially ionized atom.	3.5 + 10.2 + 13.5 = 27.2 volts.
	(7) Two ionized atoms.	3.5 + 2 × 13.5 = 30.5 volts.

If, as is generally believed, the secondary spectrum is due to the molecule and the series spectrum to the atom, then the results plotted in Figs. 2 and 3 would indicate that the higher the energy of the impacting

[1] By ionized molecule or atom is meant one from which an electron has been removed completely, leaving the residue positively charged. There seems to be no generally accepted terminology for the case of a molecule or atom in which the electron is removed to one of the outer Bohr orbits, the atom remaining neutral. Such atoms are often called "abnormal," but the verb "abnormalize" is too unattractive for use. "Partial ionization" is used here.

In the third column, the theoretical minimum energies required for each type of dissociating collision are calculated from Bohr's theory and the energy required for dissociation. The calculation refers only to the type of partially ionized atom in which the electron is moved to the second Bohr orbit. Removal to the 3d, 4th, . . . orbits of course gives other types of partially ionized atoms.

electron, the greater the ratio of the dissociating collisions to the non-dissociating collisions.

The Series Spectrum.—The atoms may return to their normal state giving out the series spectrum after having been ionized (or partially ionized) in one of two very distinct ways. One way is that contemplated in (3) to (7) of the above list. The other is that which results from an electron colliding with a *free* atom.

Free atoms however only exist under conditions where the discharge is so intense that atoms, once dissociated, can be struck again by electrons before recombining to form molecules. (Conditions of this kind predominate in some of Professor R. W. Wood's experiments on the production of the series spectrum.) The density of the electron current is, in our own experiments, probably much too low to allow impacts between electrons and atoms to be other than a negligible fraction of the total number of impacts. Hence we believe that the Balmer lines in our investigation must be attributed to impacts of types (3) to (7) in the list. If every dissociating collision resulted in completely ionized atoms (or a constant proportion of neutral and completely ionized atoms), then the radiation would be conditioned by the atom capturing a free electron. Hence the ratios $H_\alpha : H_\beta : H_\gamma : \cdots$ would have nothing to do with the energy of the electrons producing the dissociation and would therefore be constant, and the intensities (being supposedly proportional to the number of radiating units) should vary with the potential in the same way as the dissociation. One of the authors[1] found that dissociation of hydrogen began when the energy of the impacting electrons was about 13 volts and increased, very rapidly at first, until it became practically constant above about 50 volts. Since we find that the ratios $H_\alpha : H_\beta : H_\gamma : \cdots$ are not constant, and since their intensity changes do not run parallel with the amount of dissociation, the supposition cannot be true. It is therefore very likely that a large part of the dissociating collisions result in partially ionized atoms, in which the electrons are shifted to the outer orbits. The rapid changes in the ratios $H_\alpha : H_\beta : H_\gamma : \cdots$ at low voltages suggest very strongly that the higher the energy of the impacting electrons, the greater the proportion of partially ionized atoms in which the electron is shifted to orbits remote from the center. The approximate constancy of the ratios at the higher voltages need not be taken as proof that all the dissociating collisions here are now of the kind resulting in completely ionized atoms, as it may happen that the ratios of the different types of partially ionized atoms tend to a constant value at the higher voltages. What seems certain is that, especially

[1] Hughes, Phil. Mag., 41, p. 778, 1921.

at the lower voltages, dissociation into partially ionized atoms predominates. The approximate constancy of the H_α line would suggest that the number of atoms in which the electron is shifted to orbit 3 (since H_α is represented by $N(1/2^2 - 1/3^2)$) is nearly constant from 29 up to 110 volts. (It would be interesting to see whether this held between 29 and 13 volts.)

The Secondary Spectrum.—It would be natural to infer that our six lines between λ 6000 and λ 7000, which behave in the same way, originate in the same type of ionization of the molecule (whether complete or partial) and that our other six lines are to be attributed to some other type of ionization. It is exceedingly difficult to draw any useful conclusions in the absence of a satisfactory theory of the secondary spectrum. Merton and Barratt (loc. cit.) give seven different criteria for classifying the lines in the secondary spectrum, and state that many exceptions exist to any general correlation which can be laid down. It does not seem at the present moment profitable to speculate further on the origin of the various types of the secondary spectrum.

As suggested earlier in the paper, the purpose underlying this paper was to find out the variation in the distribution of energy in the hydrogen spectrum when the only variable was the energy of impact. As the effect of pressure on the distribution would be expected to diminish as it was reduced, the ideal way of conducting the experiments would be to work at very low pressures. Unfortunately, the amount of radiation given out at pressures below about .02 mm was so little with our arrangements that it would require extremely long exposures (which in turn would increase the difficulty of keeping other conditions constant) to get satisfactory spectrograms.

Preliminary experiments have been made on the effect of pressure. We plan to continue the investigation especially in the region of low voltages where the changes are most rapid, for hydrogen and other gases. In this region an equipotential source of electrons will add precision. Many investigators have worked with apparatus of this type on the critical potentials associated with the initiation of radiation (*e.g.*, the large body of work on radiating potentials), but practically nothing has been done on the quantitative distribution of radiation above these critical potentials.

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