# ON THE POTENTIAL RELATIONS IN THE STRIATED POSITIVE COLUMN OF ELECTRICAL DISCHARGES THROUGH HYDROGEN

By John Zeleny
Sloane Physics Laboratory, Yale University

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Abstract

The many lined visible spectrum from the striae in the positive column of a discharge through hydrogen must arise from electronic transitions between excited states having energy levels differing by only about 3 volts for the violet lines. The assumption made by others that the light arises from transitions to the ground level from the lowest excited state of 11.5 volts cannot hold because such transitions would give light in the extreme ultra-violet region only. It is necessary to produce excited states at least 3 volts above the lowest excited level. This requires an energy not far below the ionization potential of 16.1 volts. A process is described by which both excitation of molecules to the required levels and ionization might occur at equal intervals throughout the positive column, but a difficulty arises in the fact that the voltage drop between striae under certain conditions is found to be several volts below the ionization potential. It is assumed that the electrons acquire enough energy for ionization in these cases from collisions of the second kind with molecules of some impurity which are in excited states of comparatively low energy levels. Reasons are given for believing that the impurities involved come from the walls of the discharge tube, and that the walls play a very important role otherwise, as well.

The periodic changes in the electric force along the length of a striated positive column in a discharge tube are usually taken to indicate that there are periodic positions along the column where ionization is taking place. In fact J. J. Thomson[1] postulates that when the positive column becomes striated it does so because under the given circumstances the periodically changing field which accompanies the striated condition permits the replenishment, with the least total expenditure of energy, of the electrons lost along the path of the discharge either by diffusion to the walls of the tube or by attachment to positive ions or neutral molecules. We should accordingly expect the energies acquired by electrons between striae to correspond at least to ionization potentials.

However, the main part of the light coming from the positive column does not have its origin in the recombination of ions, for there is strong evidence[2] that there is but little recombination in the body of the gas between electrons and positive ions, owing doubtless to the high prevailing speeds of the former. Such union occurs rather at the walls of the tube.

The light from striae in a discharge through hydrogen gives a many lined spectrum and must originate then in *molecules* in excited states. The

[1] J. J. Thomson, Phil. Mag. **8**, 1 (1929).

[2] See R. Seeliger, Phys. Zeits. **30**, 329 (1929).

existence of the periodic changes of light intensity which distinguishes the striated state of the positive column points to the energy acquired by electrons between striae as that corresponding to an excitation voltage. Indeed Grotrian[3] using a stream of electrons from a hot cathode in mercury vapor has observed a striated discharge with periodic changes of potential of 4.9 volts, corresponding to the lowest excitation level of mercury. Here, however, there was no ionization occurring throughout the volume of the vapor.

When a cold cathode is used ionization as well as excitation of molecules must be taking place in the positive column and there is then a question how the two effects requiring different voltages are produced at the same equal space intervals along a discharge tube. It seems reasonable to assume that the process requiring the higher energy on the part of the electrons, i.e. ionization, determines the potential fall between the striae, and that the excitation of molecules and subsequent radiation from them is an accompanying action of this first process. According to this view when the electrons in their progress through the field have acquired enough energy for excitation some of them will begin to have inelastic collisions with molecules which raise these to excited states. This action will continue until the electrons which have as yet had no collisions of this kind gain enough energy for ionization after which both kinds of inelastic collisions will take place in the same region along the tube. The probability that at any one impact the collision of an electron with a molecule will be an inelastic one is small and hence the process given is a possible one.

The actual linear distance along a discharge tube in which the above two actions take place need be but a minor part of the whole distance between two striae since the energies required for ionization of a hydrogen molecule and for its excitation to states from which visible light may result are not greatly different. To this is added the fact that the mobility of an ion varies inversely as its motion of agitation and so when the electrons have acquired the most energy from the field their progressive speed along the tube will be the least. Accordingly many more impacts than elsewhere will here occur within a given length of the discharge tube and nearly all of the electrons will have their inelastic collisions inside a short length of the tube from which they will then begin a new excursion. Some addition must be made to this process because under some conditions the potential drop between striae is less than the ionization potential.

Compton, Turner and McCurdy[4], who have expressed views regarding the process of stria formation which in some respects are similar to those above, have assigned an important role to impurities in the gas which are so essential for the appearance of striae in nearly all gases. They postulate that the function of the impurities is, by collisions of the second kind, to restore to the stable form such metastable excited atoms which, having diffused to all parts of the interstria spaces, would otherwise after inelastic impact with comparatively slow electrons give rise to radiations there and thus tend to wash out the visibility of striae.

[3] W. Grotrian, Zeits. f. Physik **5**, 148 (1921).

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

Günther-Schulze[5] also visualizes the procedure by which the electrons in a discharge tube give up their acquired energy in inelastic impacts within periodic narrow zones in much the same way as that described above, but inasmuch as under some conditions the fall of potential between striae is less than the ionization potential he assumes that the ionization process is not related to stria formation and that ionization arises from a separate set of fast electrons evidence of whose existence has been given from spectroscopic data by Seeliger and Ôkubo.[6] Günther-Schulze believes that striae are formed as a result of the inelastic impacts in the narrow zones named of a slower set of electrons which raise the molecules to the lowest excitation level; and seeks support for this view from the fact that under some conditions the energy acquired by electrons between striae in hydrogen has a value nearly equal to this excitation potential. Unfortunately an excitation of molecules to the first levels in hydrogen does not suffice to explain the luminosity of the striae which is observed, as will be shown below.

A comparison of the magnitudes of the energies required for the ionization and for the excitation of hydrogen molecules with the measured potential drops between striae evidently deserves special consideration.

The ionization potential of the hydrogen molecule, which takes place without dissociation, is given[7] as $16.1 \pm 0.2$ volts and the energy required to raise a hydrogen molecule to the lowest excited level is given as $11.5 \pm 0.4$ volts. Above the lowest excitation level there are a large number of other levels extending according to Richardson[8] to about 15.1 volts.

In the light from striae the visible part of the spectrum must result from transitions between excited states since a transition from any excited state to the $1^1\Sigma$ state would give a line far down in the ultra-violet. To obtain the violet end of the spectrum we must start with an excited state at least 3 volts above the lowest excited level of 11.5 volts, i.e. at 14.5 volts or more.

In some recent measurements[9] I found the potential drop between striae in hydrogen at pressures below 0.5 mm to be approximately 12 volts and even lower values have been obtained by others. If in this region of pressures the electrons possess only the energy gained directly from the field between adjacent striae, how then is it possible for them to ionize the molecule or to excite it to a sufficiently high level to give rise to the visible spectral lines which are observed? It might be urged that perhaps the ionization in the gas is confined to molecules of traces of impurities having a lower ionization potential than those of hydrogen, but the argument cannot be used to explain directly the production of a hydrogen spectrum. It seems necessary therefore to invoke the aid of some other process. We might postulate, since the electrons are not able to obtain the requisite energy in the potential drop between adjacent striae, that they carry energy from one stria distance into the next,

[5] A. Günther-Schulze, Zeits. f. Physik **31**, 1 (1925).
[6] R. Seeliger and J. Okubo, Phys. Zeits. **25**, 337 (1924).
[7] Geiger and Scheel, Handbuch der Physik, Vol. 23, p. 749.
[8] O. W. Richardson, Proc. Roy. Soc. **A125**, 23 (1929).
[9] J. Zeleny, Jour. Franklin Inst., **209**, (1930).

only a part of them losing their energy by inelastic impact in any one stria. It is difficult, however, to imagine how such a process could bring about a periodic appearance of light.

It seems more plausible to assume that the electrons get the energy needed for ionization or excitation, over and above that acquired from the field within a single stria distance, by collisions with molecules of some impurity which are in an excited or metastable state requiring less energy than is requisite to excite a hydrogen molecule. There is good theoretical ground and some direct evidence[10] for the possibility of an electron having its energy increased by this sort of a collision of the second kind. By the presence of traces of impurities of different kinds and in different amounts might be explained the widely different minimum values obtained for the potential drop between striae under different circumstances and by different observers.

In support of the above view it may be mentioned that Pentscheff[11] found in very pure hydrogen that, while the potential fall in a stria diminished with reduction of pressure for a constant current, it at no time got below 20 volts, whereas in slightly impure hydrogen it fell to 13 volts under the same circumstances. The pressures used are not stated but if the lowest values of the potential which are given were obtained at pressures below 1 mm, the energy gained between striae by electrons in pure hydrogen were more than sufficient for the ionization of hydrogen molecules, whereas in the impure hydrogen it is necessary to assume that the electrons acquired some energy from secondary processes, such as the one described above, to explain the observations.

Then too, my recent measurements show that when the hydrogen gas was kept stationary and not renewed the energy acquired by electrons in their passage through a stria at any pressure is one to two volts less than when the gas in the discharge tube was being continuously renewed. We should expect a larger amount of impurity to be present in the gas in the first case cited since impurities dislodged from the walls of the tube by the action of the discharge would accumulate in the tube when the gas was not being renewed.

The amount of foreign gas liberated from the walls would naturally depend within some limits on the magnitude and time of action of the discharge current, and according to the view expressed above the potential fall between striae should accordingly diminish as the discharge current is increased. This is actually in accord with my own observations as well as those of Holm, Wehner, and Neubert.[12]

Pentscheff[11] also found a decrease in the potential fall between striae with increase of current when impure hydrogen containing mercury vapor and other gases coming from the walls of the tube was used, but when very pure hydrogen was used and great care taken by prolonged treatment to free the

[10] See H. D. Smyth, Proc. Nat. Acad. Sci. **11,** 679 (1925).

[11] P. B. Pentscheff, Phys. Zeits. **7,** 463 (1906).

[12] R. Holm, Phys. Zeits. **9,** 558 (1908); F. Wehner, Ann. d. Physik **32,** 49 (1910); P. Neubert, Ann. d. Physik **42,** 1454 (1913).

metal parts and the walls of the discharge tube of occluded impurities the potential fall between striae rather increased somewhat as the discharge current was increased.

Again, when discharges of the same current density are sent through two tubes of different diameters we might expect the amount of impurity liberated per unit surface of the walls to be approximately the same and inasmuch as the larger of the tubes has a larger ratio of volume to surface the concentration of the impurities liberated from the walls would be greater in the smaller tube. We should then expect the potential fall per stria to be smaller in the smaller tube, and this was found to be the case in my recent measurements.

When the pressure of the gas in a discharge tube is increased a discharge through the tube is less effective in liberating occluded impurities from the walls and such as are liberated form a smaller proportion of the gas than would be the case at a lower pressure. If the amount of these liberated impurities tends to decrease the potential fall between striae then this fall should decrease with decrease of pressure and such was the relation I actually found[9] both with a stationary gas and with the gas flowing continuously through the discharge tube.

Neubert[12] found that when all spectroscopic traces of mercury disappeared from the discharge through hydrogen the potential fall between striae was 11 volts at the lowest pressure used although previously when this condition was not fulfilled the values obtained were as low as 7.5 volts. Mercury molecules which appear in this instance to lower the potential fall between striae in hydrogen do not possess excitation levels low enough to account for the facts in all cases. However among other likely impurities to be found in discharge tubes there is for example oxygen whose molecules possess metastable states of energy less than 2 volts.

The evidence which has been presented in favor of the view that the liberation of impurities from the walls of the discharge tube by the current is an important factor in determining the variations of the potential fall between striae which have been observed under various conditions, is to be sure for the most part circumstantial evidence.

In connection with the experimental result that the energy acquired by electrons in their motion between two striae increases as the pressure increases, it should be emphasized that there is evidence which indicates that electrons in collisions with molecules may lose more energy than would result from purely elastic collisions and which loss alone I considered in computing the energy acquired by electrons from the observed potential fall between striae. By such greater losses if of the proper magnitude might be explained the increase with pressure in the observed potential drops between striae, but the assumption of these larger losses introduces other difficulties and does not help to explain most of the other observed variations studied.

Another factor that may have some influence on the striated discharge consists of the gas convection currents always present in these discharge tubes. It is believed however that most of the causes that affect distances and potential drops between striae center about the walls of the tube. These walls, under electronic bombardment during a discharge or with change of pressure or temperature, release occluded molecules of the principal gas and those of foreign substances. They destroy the metastable states of molecules which impinge upon them. They are the seat of the main portion of the recombination of ions and electrons which occurs in the discharge tube, giving rise thereby to electric currents from the axis of the tube towards these walls. Electric charges which collect on the walls influence the electric field in the neighboring gas; and electrons in collision with the walls may lose more or less of their energy depending on the state of the surface of the walls. The differences between the numerical results of different observers on stria distances and the potential fall between striae in discharge tubes can best be accounted for by assuming them due to effects of different conditions at the walls of the tubes. Full equilibrium conditions at the surface of these walls are at best very slow of attainment especially where the gases inside of the body of the glass are concerned. Even if by special treatment such an equilibrium is attained and concordant results obtained in a given case, the nature of the essential elements in equilibrium might still remain unknown.