THEORY AND EXPERIMENTS RELATING TO THE STRIATED GLOW DISCHARGE IN MERCURY VAPOR

By K. T. Compton, Louis A. Turner and W. H. McCurdy

Abstract

Theory of the glow discharge in a monatomic gas.—For the case of parallel plane electrodes with a hot cathode as source of electrons, the potential distribution and ion concentration in the Crookes dark space, negative glow, Faraday dark space and positive column are shown to be predictable from considerations of space charge and of ionization and excitation of the gas. While with weak currents there is a negative space charge throughout, sufficiently intense ionization is shown to lead to a cathode drop, followed by a region of reversed electric field in which positive ions and electrons both move toward the anode by diffusion, owing to their large concentration gradient. Still farther from the cathode the field changes to its normal direction and increases up to the positive column. In the positive column the field and concentration are uniform unless atoms excited by electron impacts in certain layers are prevented from diffusing between the layers, when *striations* may be obtained with periodic changes of field and of concentration. The cathode edge of each striation has a positive space charge. The *theory of the arc discharge* is essentially the same, the arc being simply the negative glow of the longer glow discharge.

Glow discharge in mercury vapor.—Various predictions of the above theory were verified by experiments with Hg vapor in vacuum tubes provided with hot cathodes. (1) *Potential distribution and ion concentration* were investigated by Langmuir's modified probe method and found to agree with the theoretical deductions, except that the concentration of positive ions in the positive column comes out too large. This result indicates the *presence of negative mercury ions.* (2) *The distribution of velocities of electrons* is Maxwellian except between striations. (3) *The emission of light* seems associated more with excitation by electron collision than with ionization and recombination. (4) *Conditions for existence of striations.* Striations are not found in pure Hg vapor unless the current is small or some substance like H_2 is introduced to remove excited atoms. (5) The presence of atomic hydrogen which should be produced in the process of removing excited Hg atoms was proved by use of tungsten oxide. (6) Introduction of He, which cannot remove excited atoms, does not tend to produce striations. (7) *The relative concentrations of excited atoms* was determined from the optical absorption of subordinate series Hg lines. It was found that excited atoms exist in striations but not in the regions between, and are more numerous if the amount of H_2 impurity is reduced.

Band spectrum of HgH seems associated with the action of excited Hg atoms on hydrogen, and is emitted as a result of inelastic collisions in striations.

A. Theoretical

THEORETICALLY it should be possible to derive an equation to describe completely the phenomena in glow discharges. Sir J. J. Thomson outlined a method of attack in which he considered the effects of ionization, recombination, mobility, diffusion and space charge.[1] Unfortunately he was able to obtain solutions of the equations only in very restricted cases, even though the equations were much less general in form than they should be to include a number of phenomena which have only recently been understood.

We have, therefore, made an attempt to apply purely physical considerations of a rather qualitative nature and have succeeded in arriving at certain conclusions which are supported by experimental tests and which give an apparently satisfactory explanation of the essential features of the glow discharge in mercury vapor. Probably similar considerations hold for other monatomic gases.

We shall suppose that our discharge tube is supplied with a hot cathode as a source of electrons, in order to reduce the problem to its simplest terms. This avoids the complication present in dealing with a cold cathode, arising from the necessity of a cathode drop which is sufficiently large to cause emission of electrons from the cathode by positive ion bombardment in sufficient number to maintain the discharge. Our case depends only on the properties of the gas and presents all the essential features of glow discharges.

(1) CATHODE DROP, NEGATIVE GLOW, FARADAY DARK SPACE

Consider first the effect of ionization upon the potential distribution between a hot cathode source of electrons and some region of the gas distant d (such as a near-by anode) maintained at a positive potential V_a which is greater than the ionizing potential of the gas V_i. For the sake of simplicity we shall consider plane parallel electrodes; similar reasoning would apply to electrodes of any shape.

Curve 1, Fig. 1, shows the linear distribution of potential which would exist in the absence of space charge, i. e. if the electron emission from the cathode were suppressed. Curve 2 shows the distribution which would exist if the electron emission occurred as limited by its own space charge but with ionization suppressed. The existence of negative space charge results in a positive curvature at every point, and the exact shape of the curve is determined by the density of this space charge at every point, together with the fact that the initial and final points are fixed and the curve is horizontal at the origin.

Suppose, now, that a definite small amount of ionization is allowed at the point where the electrons have fallen through the ionizing potential V_i. The positive ions thus formed will be drawn toward the cathode

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[1] J. J. Thomson, Conduction of Electricity through Gases.

and will neutralize the negative space charge of $A\sqrt{M/m}$ times their number of electrons, where A is a constant greater than, but of the order of, unity. A would be $4\sqrt{2}$ if positive ions and electrons were in thermal equilibrium in the electric field,[2] it would equal $2^{5/4}$ if both collided inelastically at every impact with a gas molecule.[3] In general $A\sqrt{M/m}$ is equal to the ratio of the average velocity of advance of the electrons to that of the positive ions and will have different values in different parts of the discharge, except in the case of a very long discharge with uniform potential gradient. In particular, very close to the cathode the electrons are moving away relatively slowly, while the positive ions are moving rapidly, so that the value of $A\sqrt{M/m}$ diminishes to its minimum value as the cathode is approached. Now it is just at the surface of the cathode that the limitation of emission by space charge is effective, the current being such as to make the electric intensity zero at this point.[4]

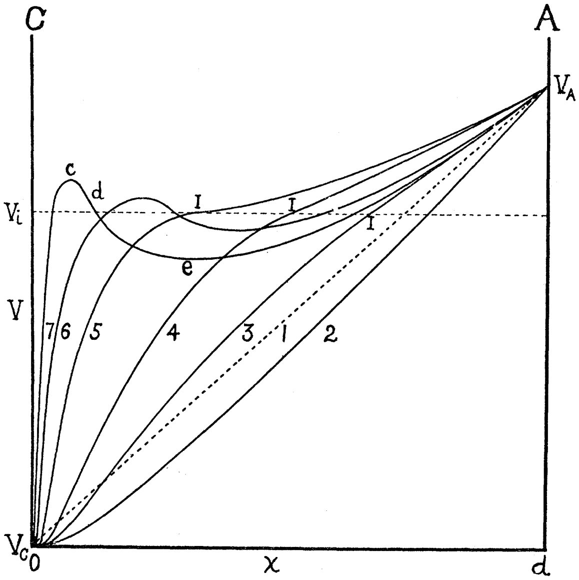

Fig. 1. The effect of increasing amounts of ionization on the distribution of potential between two parallel electrodes, one of which is a source of electrons. Curve 1 shows the electrostatic distribution, curve 2 the distribution in the presence of space charge from the electrons, and the remaining curves the distributions in cases of successively increasing amounts of ionization at the ionizing potential V_i.

[2] K. T. Compton, Phys. Rev. **21**, 276 (1923)

[3] K. T. Compton, Phys. Rev. **7**, 492 (1916), equation (9)

[4] We are neglecting corrections due to initial velocity of emission (Langmuir, Phys. Rev. **21**, 419, 1923) which would complicate the argument but would not change the conclusions to be reached.

Thus the increase in the electron emission which results from the ionization is determined by the value of $A\sqrt{M/m}$ near the surface of the cathode, being just sufficient to neutralize the charge of the positive ions there, but insufficient to neutralize it in regions farther away. The final result, therefore, is to leave a zero electric intensity and a negative space charge at the surface of the cathode, with a diminishing negative space charge, which may be replaced by a positive space charge if the ionization is sufficient, at greater distances. Such a condition is shown by Curve 3, in which the space charge is positive (curvature negative) between the point I at which ionization occurs and another point closer to the cathode. Between I and the anode the space charge is negative, and more so than in Curve 2 because of the larger electron current. Since the curvature is governed by the space charge at each point and the two end points are fixed, the potential distribution curve is uniquely determined. The result of the ionization is to concentrate most of the potential drop into a region nearer the cathode.

If the amount of ionization be increased, these changes in the potential distribution will be magnified, as shown in Curves 4 and 5. Although the potential gradient between the point I and the anode is diminished, the concentration of electrons must be more than proportionally increased, so as to carry the increased current.

Further increase in the amount of ionization leads inevitably to a potential distribution of the type of Curves 6 and 7, for increased ionization gives increased space charge and hence increased curvature. With fixed end points, large negative curvature near the cathode and large positive curvature near the anode can be satisfied only by a line with a maximum and a minimum.

At first sight the possibility of a reverse electric field is difficult to accept, and it is quite at variance with the theoretical attempts which have hitherto been made to explain the discharge. In the region of the negative field the current is obviously not due to the electric field; it can only be a *diffusion* current caused by a large concentration gradient of ions, both positive and negative. In earlier theories of the discharges, diffusion has been considered to be of secondary importance and generally neglected in order to simplify the equations. The actual explanation of this feature of the discharge appears to be as follows:

The region of ionization is a region of maximum concentration of ions of both signs. There exists, therefore, a force due to a partial pressure gradient proportional to dn/dx (where n is the number of ions of either sign per unit volume) tending to move the ions toward the regions of less concentration. The magnitude of this force acting on the ions in unit volume is $-kT(dn/dx)$, where kT is two-thirds the mean kinetic energy of the ions. At the same time there is a force on these ions, due to the electric field E, equal to neE. The resultant force on the ions of either sign, per unit volume, is

$$F = neE - kT(dn/dx)\cdot \qquad (1)$$

Between the region of ionization and the cathode these two forces are always in the same direction for positive ions and in opposite directions for electrons, but the first term must always predominate, else the discharge would cease.

Between the region of ionization and the anode, the conditions are more complicated. If the ionization is weak, the second term is small, all electrons move toward the anode and no positive ions enter this region. If the amount of ionization is increased, the first term is diminished because of the concentration of potential drop near the cathode, while the term due to diffusion is increased. With sufficiently intense ionization, the force due to diffusion exceeds that due to the electric field and we then have *both electrons and positive ions drifting toward the anode from the region of ionization.* This latter condition tends to produce a reverse electric field in the region of the concentration gradient, on account of the greater mobility of the electrons. We have, in effect, a diffusion cell[5] in which the electrons drift faster than the positive ions towards the anode and set up a negative space charge near the anode, leaving a positive space charge behind, and setting up an electric field which accelerates the positive ions and retards the electrons so that they drift at the same rate. If the positive ions and electrons are present in concentrations which are large compared with their difference (as is shown experimentally to be true in this region, by interpreting the potential gradient by Poisson's equation), this reverse electric field is of such magnitude as to give a potential difference

$$V_1 - V_2 = \frac{kT}{e}\,\frac{\mu_- - \mu_+}{\mu_- + \mu_+}\log\frac{n_1}{n_2} \qquad (2)$$

between any two points 1 and 2. μ_- and μ_+ are the mobilities of the electrons and positive ions, respectively.

Thus far we have not considered recombination between electrons and positive ions. The rate of recombination is proportional to the product of the concentrations of the electrons and positive ions, and is therefore maximum in the region of maximum concentration c, Curve 7.

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[5] Wood, de Long and Compton, Phil. Mag. **32,** 499 (1916)

As the ions diffuse toward the anode, they continually recombine and thus the concentration gradient is larger than it would otherwise be. Equation (2) still holds, but the ratio n_1/n_2 is increased by recombination.

Now there must always be an *excess* of current carried by electrons, to account for the current actually flowing in the tube. Near the point *c*, Curve 7, this excess is small compared with the total amount of electricity of both signs moving toward the anode. Farther on, toward *d*, the total ion concentration has been reduced by recombination, and as the anode is further approached the positive ions have so largely disappeared by recombination that the space charge becomes negative at *d*. From this point to the anode the potential distribution curve has positive curvature and the field is in the normal direction beyond a point of minimum potential, *e*.

Such is the physical picture of the phenomena near the cathode which seems to be the inevitable consequence of the properties of the ions. The only condition necessary to secure this type of discharge is intense ionization, which is insured by a sufficient applied potential difference, a cathode sufficiently hot to supply the electrons and a gas at any pressure not so low as to give too infrequent collisions nor so high as to cause electrons to reach their terminal speeds at speeds below that necessary for ionization.[6] These are the conditions for a glow discharge. When they are not met we have a discharge with very much smaller current and negative space charge throughout.

The cathode drop is the potential drop between the cathode and the region of maximum ion concentration. It must exceed the lowest potential at which the gas can be ionized. The negative glow is that region in which recombination is rapid. The glow is therefore of maximum intensity in the region of maximum ion concentration and fades out gradually toward the anode. The Faraday dark space is simply that region in which the glow from recombination is faint, owing to paucity of ions. The Crookes dark space is the region near the cathode in which recombination is infrequent on account of the strong field and the high speed of the ions. A confirmation of the above distinction, or lack of distinction, between the negative glow and the Faraday dark space is found in the fact that no abrupt change in intensity of spectral lines is found as they are followed out from the one region into the other.

OSCILLATING DISCHARGE

Consideration of conditions immediately outside the cathode leads to the conclusion that the current through the discharge may be of an

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[6] Compton, Phys. Rev. **22**, 333 (1923)

oscillatory or interrupted nature if the external resistance in series with the discharge is large and the ionization intense. This is evident from the fact that, if the ionization is so intense as to give a supply of positive ions sufficient to create a positive space charge clear up to the surface of the cathode, then the electron emission necessarily increases to the saturation value determined by the cathode temperature, and the increased potential drop across the series resistance may reduce the drop across the discharge to a value too small to maintain it. The current then diminishes, with redistribution of potential, the discharge builds up again, and the cycle is repeated. Such a process is discussed in some detail for the case of low voltage arcs in a recent paper.[7]

(2) Positive Column and Striations

Now consider the region nearer the anode in a long discharge tube, Fig. 2. We have seen that the big concentration gradient to the right of *c* diminishes as we proceed toward the anode and the positive ions disappear through recombination, leaving, beyond *d*, a negative space charge and a potential distribution curve which is concave upward. At some point along this curve, such as *f*, the electrons must again acquire sufficient energy to ionize the gas. This is inevitable because of the continual increase of electric field shown by the positive curvature. It is also necessary in order to satisfy Poisson's equation, whose application shows that positive and negative ions must exist in nearly equal concentrations at any given point in the discharge, except within the cathode drop. Thus the electric field increases toward the anode until at some point *f* it is sufficient to cause just enough ionization to compensate for the loss of positive ions through recombination and diffusion to the walls of the tube. In this equilibrium condition the concentrations of positive ions and electrons must be equal, so that the potential distribution curve is straight and continues with constant gradient up to the close vicinity of the anode. This region *f-a* is the positive column. At some point between *d* and *f* the concentration of positive ions reaches a minimum.

Under certain conditions, to be discussed later, the positive column is striated. We venture to propose the following explanation of the striations, based upon the effect of inelastic impacts upon the mobility of the electrons and, therefore, upon the potential distribution.

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[7] Eckart and Compton, Phys. Rev. **24**, 97, 1924.

Suppose that an electron collides inelastically with a molecule at some point such as h, Fig. 2. Now the mobility of an electron is given by the expression[8]

$$\mu_{-} = 0.815\,(el/mc)\ , \tag{3}$$

where l is the mean free path and c is the root mean square translational speed. Evidently the electron mobility is minimum just before it has acquired sufficient speed to collide inelastically and maximum immediately after this collision. The contribution of the electron to the negative space charge varies inversely as its mobility, so that the effect of the inelastic collision is to cause an abrupt decrease in negative space charge. As the electron again acquires speed, its mobility diminishes, its contribution to the negative space charge increases, and finally the process is repeated at another inelastic impact nearer the anode. Since the positive column is, on the average, a region of zero space charge, these variations produced by successive inelastic impacts must give rise to alternate regions of positive and negative space charge, as indicated by the heavy curve of Fig. 2.

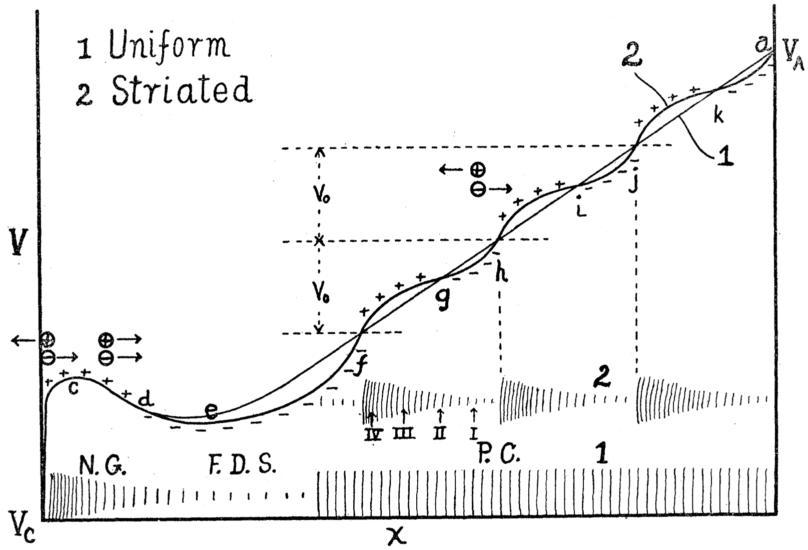

Fig. 2. The theoretical potential distribution in the case of a long discharge tube and the effect of inelastic impacts at points f, h and j on the potential distribution and space charge. Arrows indicate the direction of average drift of ions in various parts of the discharge.

The important feature of these variations in electric intensity is that they are such as to increase the probability that other electrons will

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[8] Townsend, Electricity in Gases, p. 84.

collide inelastically in the same regions. This is because of the increased electric intensity in the region of an inelastic impact. Thus we have the condition that one inelastic impact tends to cause other inelastic impacts in the same region, which is just what is needed to account for striations. Given, therefore, electrons moving in a field through a gas in which impacts are elastic below a certain speed and inelastic above it, we are led to the conclusion that there will be successive regions in which the inelastic impacts will be concentrated, that the potential drop between these regions will be that necessary to enable the electrons to acquire the critical speed for inelastic impact and that the regions of inelastic impacts will be characterized by positive space charge and will be separated by regions of negative space charge. Since inelastic impacts produce excitation or ionization of the gas molecules, the regions of inelastic impact will be regions of maximum luminosity. It should also be noted that the production of positive ions by inelastic impacts adds to the positive space charge of the region in which they occur, thus accentuating the influence of the inelastic impacts. On account of recombination, the positive ions are present in deficient numbers in the intervening negatively charged regions. This effect of the positive ions, however, is *not essential* to the existence of striations, as shown by Grotrian's[9] observation of striations in mercury vapor in the absence of ionization.

Thus, from fundamental properties of electrons, ions and molecules, we have been led to infer a potential distribution as indicated in Fig. 2, and to conclusions regarding distribution of luminosity, space charge and ion concentration. The experiments to be described below confirm these inferences in every detail.

COMPLICATING EFFECT OF EXCITED ATOMS

An additional factor enters to complicate the situation in the case of a gas, like mercury vapor, which may exist in excited states, especially if some of these states are metastable or otherwise of long duration. Suppose that electrons collide inelastically with normal mercury atoms in the region *h*, Fig. 2, and put these atoms in an excited state. Those electrons cannot again collide inelastically with normal mercury atoms until they have moved to *j*, distant one critical potential difference from *h*. But if the excited atoms produced at *h* and *j* can diffuse into the intervening space, electrons may collide inelastically with them almost anywhere in this space, since there are a large number of stages of higher excitation into which the previously excited atoms may be put at another impact,

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[9] Grotrian, Zeits. f. Phys. **5**, 148 (1921)

and some of these may be produced after the electron has fallen through only a small potential drop. Thus, whereas inelastic impacts can occur only at intervals of a critical potential in the case of normal atoms alone, they may occur almost anywhere if numerous excited atoms are present in addition to the normal atoms. In order to have sharply defined striations, therefore, it is necessary to have so small a number of excited atoms between the striations as to make it improbable that electrons will collide with them. Such a small concentration of excited atoms is realized either by using very small currents or by mixing with the gas some other gas which has the property of causing the disappearance of excited atoms. Both of these deductions are confirmed by the following experiments with mercury vapor.

B. EXPERIMENTAL

In order to test the foregoing theory the following series of experiments were performed. The tests of the last part of the theory will be described first.

(1) EFFECT OF EXCITED ATOMS ON EXISTENCE OF STRIATIONS

It was immediately found, as had been known before in other cases, that the positive column in mercury vapor is *uniform* if the vapor is free from impurities (except in the particular case of currents too small to give a cathode drop, in which case the luminosity in the striations is the continuous band spectrum of Hg_2 arising from temporary molecular combinations of excited mercury atoms[10]).

If a trace of hydrogen is added to the mercury vapor, striations appear if the current is low but spread out and blend into a uniform positive column as the current is increased. If more hydrogen be added, the striations persist to larger currents, but ultimately merge as before when the current is further increased.

In order to show that the action of the hydrogen is really to reduce the concentration of excited atoms, an experiment was carried out in which the concentration of excited atoms in various parts of the discharge was tested by their optical absorption of sharp and diffuse series lines of a mercury arc. The arrangement is shown in Fig. 3.

Light from a cooled quartz mercury arc Q was focussed by a quartz lens L_1 on the axis of the quartz tube AF in which the discharge was maintained in mercury vapor at any convenient pressure, which could be

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[10] Grotrian, loc. cit.[9];
Franck and Grotrian, Zeits. f. Phys. **4**, 89 (1921)

regulated by the temperature of a surrounding electric oven, not shown. The light passing through the tube was focussed on the slit of a Hilger quartz spectrograph, and its spectrum photographed. Comparison of alternate exposures with the discharge in *AF* first on and then off, indicated that the subordinate series lines ending on $2p_1$, $2p_2$ and $2p_3$ were strongly, and about equally, absorbed by the luminous vapor, but not by the unexcited vapor. The degree of this absorption is a measure of the concentration of excited atoms.[11]

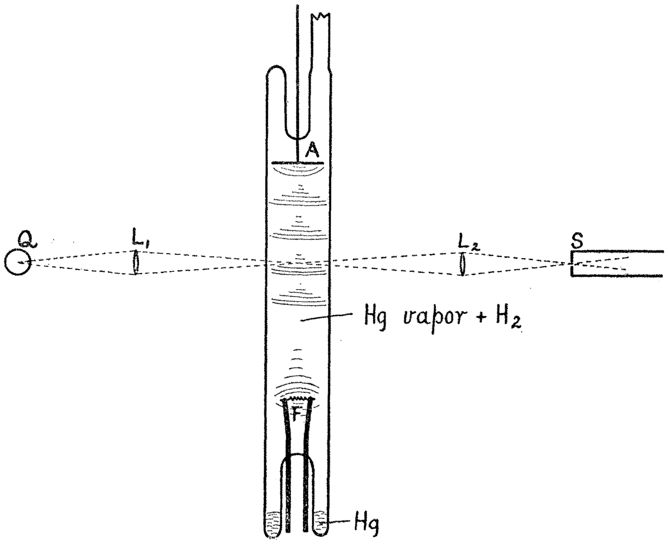

Fig. 3. Arrangement of apparatus for the study of the distribution of excited Hg atoms in various parts of the discharge. The concentration of excited atoms was taken to be proportional to the absorbing power for subordinate series lines.

In confirmation of the theory, it was found that the regions between striations did not detectably absorb these lines, the striations did absorb them, and the absorption was greatly increased if the amount of hydrogen was diminished.

A second experiment was devised to show that the action of the hydrogen was really to get rid of the excited atoms, and not something else. A discharge tube of the form shown in Fig. 4 was arranged horizontally and in it was placed a long glass boat *MN* containing tungsten oxide W_2O_3. This is a yellow powder which turns blue when reduced, and is known not to be reduced by molecular hydrogen at the temperatures involved in the present experiment. Langmuir[12] has shown that

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[11] A complete report of various spectroscopic observations of the emission and absorption spectrum is to be published later.

[12] Langmuir, J. Am. Chem. Soc. **35**, 931 (1913)

this oxide is reduced by *atomic* hydrogen, and Cario and Franck[13] and Duffendack and Compton[14] have used such reduction to prove the dissociation of hydrogen which occurs in the presence of excited mercury atoms.

On the present theory, the excited atoms are produced in the luminous striations. Those which do not revert to the normal state through radiation may do so by expending their energy to effect the dissociation of hydrogen molecules with which they collide. We should therefore expect to find an excess of atomic hydrogen in the region of the luminous striations and to detect this atomic hydrogen by its reducing action on the tungsten oxide. This was actually done. The blue patches which appeared on the surface of the oxide corresponded in position with the luminous striations. They were not as sharply defined as were the striations, owing, without doubt, to the diffusion of the atomic hydrogen away from its place of production. Rather intense discharges were necessary to give detectable reduction before the whole surface became rather uniformly reduced by atomic hydrogen from the region of the filament. Nevertheless the results were in conclusive support of the theory.

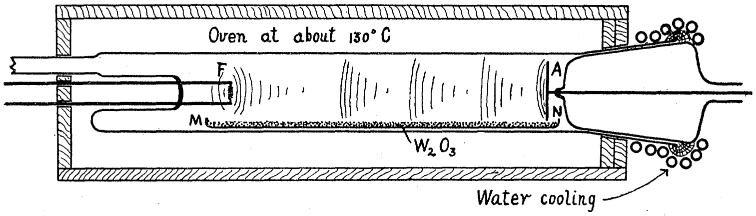

Fig. 4. Apparatus by which it was proved that hydrogen is dissociated most rapidly in the luminous regions of the striations. The atomic hydrogen was detected by its reduction of tungsten oxide, and its formation was ascribed to collisions of the second kind with excited mercury atoms.

In this connection it may be noted that, although no hydrogen lines are found, the striations show strongly the band spectrum of HgH,[15] which is evidently associated with the action of excited mercury atoms on hydrogen, although it is not in the process of dissociation that the radiation from HgH occurs, since we failed entirely in an attempt to excite this spectrum by strongly illuminating with 2536 resonance radiation a mixture of mercury vapor and hydrogen. Apparently the HgH

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[13] Cario and Franck, Zeits. f. Phys. **11,** 161 (1922)

[14] Duffendack and Compton, Phys. Rev. **23,** 583 (1924)

[15] Turner and Compton, Phil. Mag. **48,** 360, 1924.

molecules may be formed in the presence of excited atoms but require additional excitation to produce the band spectrum.

Finally, an experiment was tried to clinch the argument. According to the theory, an impurity is effective in producing striations only because it acts to decrease the concentration of excited atoms. Hydrogen does this because the energy of the excited mercury atoms (4.7 to 5.5 volts) is sufficient to dissociate hydrogen molecules, either at collisions of the second kind or by actual chemical oxidation. If helium were used in place of hydrogen, we should not expect it to have any effect on the excited atoms, since they would need about 20 volts energy to produce any change in a helium atom. So we mixed pure helium, in place of hydrogen, with the mercury vapor and found that the positive column remained unchanged and uniform for amounts of helium up to more than a thousand times the amount of hydrogen that would have been effective in causing striations. Still larger amounts of helium did produce a tendancy to striations, which may have been due to traces of impurity in the helium or to collisions of the second kind of the sort in which the energy of the excited atom is transformed into kinetic energy of the impacted molecule.

(2) Potential Distribution and Ion Concentration

To study potential distribution and ion concentration in the discharge the method recently devised by Langmuir[16] was employed, as being the most powerful one available and free from errors inherent in the older, exploring electrode method. The results of this study are being published in detail by one of us[17] and will therefore be discussed but briefly here. A short length (about 3 mm) of 4 mil tungsten wire, projecting from the tip of a fine glass tube, served as the exploring electrode and could be moved to any position between the hot filament cathode and the anode of the discharge tube. It was connected, through a multi-range millivoltmeter, to a potential divider by which its potential could be adjusted to any value relative to the anode or the cathode. When its potential V is negative with respect to that of the gas V_0 in the immediate vicinity, the negative current density to it is, approximately

$$I = I_- - I_+ \tag{4}$$

$$I_- = ne\sqrt{\frac{e\overline{V}}{3\pi m}}\,\epsilon^{-3(V_0-V)/2\overline{V}} \tag{5}$$

$$I_+ = Ne\sqrt{\frac{e\overline{V}_+}{3\pi M}} \tag{6}$$

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[16] Langmuir, Science **58,** 290 (1923); Gen. Elec. Rev. p. 731 (1923)

[17] McCurdy, Phil. Mag. **48** (1924)

where I_- and I_+ are the currents of electrons and of positive ions, respectively, reaching the electrode, n and N are the numbers per unit volume of electrons and positive ions, m and M are their masses and $\overline{V}$ and $\overline{V}_+$ are their average energies in equivalent potential drop. Eqs. (5) and (6) assume Maxwellian distributions of velocities and Eq. (6) is subject to corrections involving the radius of the positive ion sheath which surrounds the electrode, for which the reader is referred to the more complete report of this phase of the work.

The experimental procedure is to determine I_+ by measuring I at some value of V so negative that I_- is negligible. This, with the correction noted above, gives the value of I_+ appropriate to any value of V less than V_0. Knowing I_+, it is added to any value of I to obtain the corresponding I_-. Then, if the logarithms of these values of I_- are plotted against the corresponding values of V, a straight line is obtained, for, from Eq. (5)

$$\log I_- = \log\left(ne\sqrt{\frac{e\overline{V}}{3\pi m}}\right) - \frac{3V_0}{2\overline{V}} + \frac{3V}{2\overline{V}}\,. \tag{7}$$

It is to be noted that this equation holds only for $V < V_0$. If $V > V_0$, the space charge around the electrode is negative instead of positive and the current is subject to a different law. Thus a "break" in the log I_--V curve indicates the point at which $V = V_0$ and therefore gives V_0, the potential of the gas. The slope of the straight line is $(3/2\overline{V})$ and therefore gives the average energy $\overline{V}$ of the electrons. The ordinate at $V = V_0$ is $\log\,(ne\sqrt{e\overline{V}/(3\pi m)})$ and enables the number n of electrons per unit volume to be calculated. Similarly, from Eq. (6), if the average energy $\overline{V}_+$ is estimated from mobility considerations, or otherwise, the concentration of positive ions can be calculated.

Fig. 5 gives four typical experimental log I_--V curves, taken at positions noted in the upper left hand corner, and also in Fig. 2. The circles in each case represent the point at which $I_- = I_+$, i.e. the point which would have been taken as the potential of the region by the old exploring electrode methods. The true potentials are given by the discontinuities, marked with arrows. That this interpretation of the discontinuities is correct was checked by a second method, also suggested by Langmuir, in which the exploring electrode was a short, 1 mil tungsten filament of hairpin form, which could be heated by closing a switch in a battery circuit. The true potential of the region is found by decreasing the potential of the filament from a positive value to the least potential at which the current to the filament is independent of its temperature, for, at any lower potential, thermionic emission occurs and at higher potentials it is suppressed. The two methods gave identical results for the potential of the space.

Neglecting a small error at the bottom, amounting to only a few per cent of the total current and probably due to an approximation in making the correction noted above, Curves III and IV (Fig. 5) are straight lines showing that we have a Maxwellian distribution of velocities among the electrons in the regions of glow in the striations, at least for velocities below the critical velocity for inelastic impact. Curves I and II show that there is a departure from a Maxwellian distribution in the dark spaces between striations. This departure is probably accounted for by the fact that the electrons which start with a Maxwellian distribution in the striations, fall through nearly equal potential differences before they collide inelastically in the next striation. If all fell through exactly the same potential difference, the electrons with the Maxwellian distribution shown by Curve A would reach the next striation with a distribution shown by Curve B. Owing to the fact that the electrons may collide inelastically whenever their speed exceeds the critical speed (about 5 volts) and that not all inelastic impacts occur exactly in the same region,

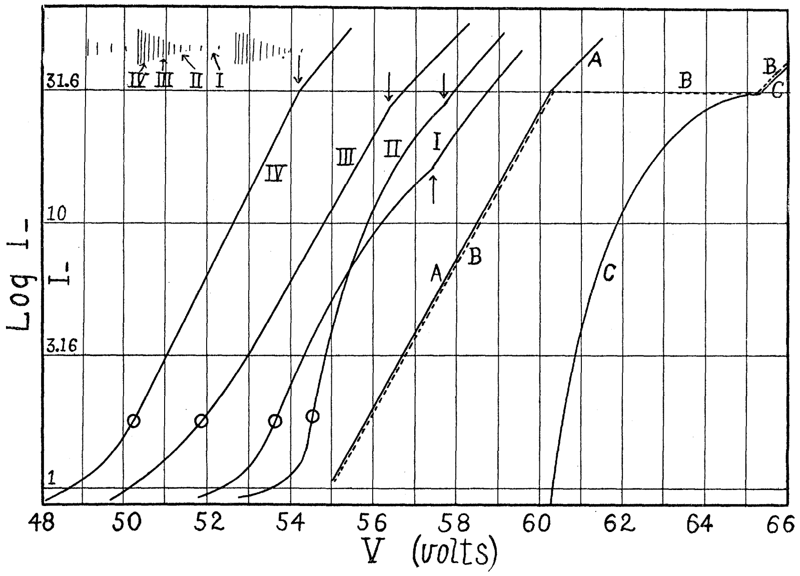

Fig. 5. Curves I, II, III and IV show the electron current to an exploring electrode placed in the parts of a striation noted in the upper left corner of the diagram. The arrows indicate the potentials of the region with respect to the cathode, and from the curves the mean kinetic energy and concentration of the electrons may be calculated. Curves A, B, C illustrate the cause of the departure of the experimental curves from straight lines in the dark spaces between striations.

the actual distribution curve just in front of a striation would be expected to be suppressed at the higher velocities and rounded off like Curve C, which is the type of the observed curves in this region.

We are led thus to the conclusion, in agreement with our theory, that most of the inelastic collisions occur in the striations and that the energy requisite for inelastic impacts is gained in the potential drop between striations.

Furthermore, we are led to the interesting and significant conclusion that *a region of ionization gives a Maxwellian distribution of velocities to the electrons in this region.* The mechanism producing this distribution is not yet clear. It is known on dynamical grounds that such a distribution results from sufficiently numerous collisions, but this cannot be the complete explanation here, else there would be no reason for not anticipating a Maxwellian distribution also in the dark spaces between striations. This conclusion is also in agreement with observations of Langmuir and Jones,[18] who found Maxwellian distributions of velocities among electrons in a region of intense ionization where, however, the mean free path was so long in comparison with the dimensions of the apparatus that an explanation on the basis of momentum transfers at collisions is impossible.

It should be mentioned that our experiments showed Maxwellian distributions everywhere in the Faraday dark space and negative glow except within the region of the cathode drop, which we could not investigate on account of its small thickness.

The potential distribution in the discharge in one typical case is shown in Fig. 6, together with the electron and positive ion concentrations in various regions. It is seen that there is exact agreement with the predictions of the theory as to ion concentration, regions of positive and negative space charge and general shape of the potential distribution curve. Mechanical difficulties prevented the continuation of these curves clear up to the cathode and anode.

The potential drop between striations is very close to 5 volts, which indicates that the ionization occurring in the positive column is of the cumulative type. Evidently the majority of inelastic impacts result in the formation of excited atoms and only the relatively small number of inelastic impacts with previously excited atoms may result in ionization.

Table I gives numerical results of one set of measurements, with calculated values of electron energies and of electron and ion concentrations. The calculations of positive ion concentrations were made from

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[18] Langmuir and Jones, Science **59**, 380 (1924)

Eq. (6), using values of the mean energy of the positive ions computed from the ordinary mobility equation, with the aid of the observed values of the potential gradient. This calculation involves considerable uncertainty, which probably accounts in part for the apparent excess in the number of electrons over positive ions in the Faraday dark space, an excess much larger than is possible to reconcile with Poisson's equation. Yet the order of magnitude of the values should be correct. The values for the electron concentrations involve no such uncertainty, and should be quite reliable.

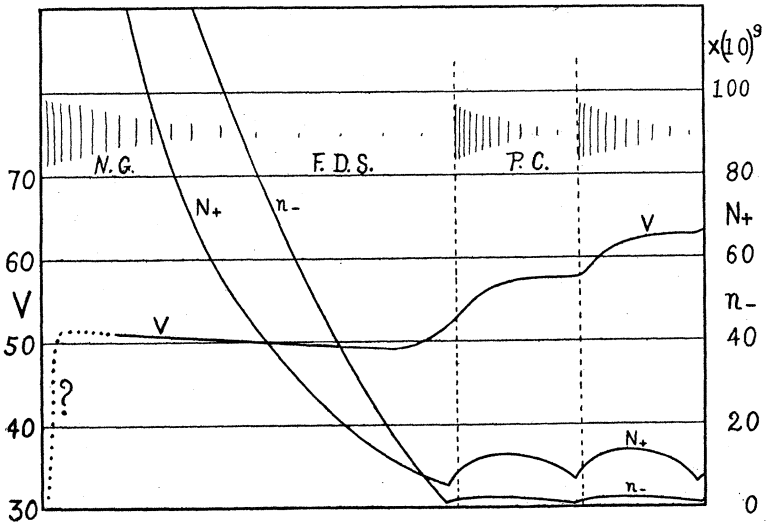

Fig. 6. Experimental values of electron concentration *n*, positive ion concentration *N* and potential *V* in various parts of the discharge. The values of *N* are rough approximations, but the values of *n* and *V* should be quite accurate.

TABLE I

V_0 is the potential of the gas with respect to the cathode;
$\overline{V}$ is the mean energy of the electrons, in volts;
n and *N* are the concentrations of electrons and positive ions, respectively.

Position	V_0	$\overline{V}$	*n*	*N*
Between striations	57.4	1.2	0.38 $(10)^9$	10.0 $(10)^9$
Anode side of striation	57.3	1.5	0.75	11.8
Middle of striation	56.6	1.4	1.30	12.4
Cathode side of striation	54.2	1.7	1.55	11.0
1.3 mm. into Faraday dark space	51.7	1.5	0.65	5.6
13 mm into Faraday dark space	49.2	0.40	21.0	15.5
20 mm into Faraday dark space	49.6	0.24	53.5	26.2
Anode side of negative glow	50.0	0.40	101	51.2
Middle of negative glow	50.1	0.91	130	900

(3) Existence of Negative Atom-ions

The concentration of positive ions N exceeds that of electrons n in the positive column by amounts which seem to be too large to be accounted for by an uncertainty in the manner of calculation. It is easily shown that this apparent difference is enormously larger than is allowable by Poisson's equation. The only reasonable explanation seems to be that there exist negative ions of atomic mass in concentration comparable with that of the positive ions. Such ions would not have been detected in the present experiments, since they would carry but an insignificant portion of the negative current, owing to their large mass relative to that of the electrons. In support of this hypothesis it may be mentioned that several other phenomena have pointed to the same conclusion, and that Franck and Grotrian[10] have shown theoretical reasons for expecting excited atoms to possess electron affinity and to form fairly stable negative ions. A direct experimental search for such negative ions of monatomic atoms is being undertaken.

(4) Mechanism of Light Production

These experiments prove, incidentally, that the greater part of the light produced in the glow discharge comes, *not from recombination* of ions and electrons, *but from excitation* of neutral atoms by electron impacts. If light were produced only by recombination of ions and electrons, we should expect the light from the negative glow to be several thousand times as intense as that from the positive column, since the rate of recombination is proportional to the product of the concentrations. On the contrary, the positive column is actually observed to be brighter than the negative glow. It seems safe to conclude, therefore, that practically all the light from the positive column comes in the process of readjustments within the atoms following excitation, or partial ionization. The different character of the light from the negative glow is probably due to the contribution of light from ion recombination in this region, giving a different distribution of energy in the spectrum.

(5) Relation of Glow Discharge to Arc

On the basis of the foregoing analysis of the conditions in a glow discharge from a hot cathode, there is no reason for drawing a sharp distinction between the glow discharge and the arc from a hot cathode. The distinction seems to be purely a matter of distance between the electrodes. If this distance is so small that the ions produced just beyond the cathode drop diffuse toward the anode, recombining on the way, and are still present in large concentration at the anode, then the discharge shows no positive column, and is of the arc type. In other words, if, in Fig. 2, the anode were placed to the left of the point *f*, the conditions between it and the cathode would be the same as shown except for secondary local effects due to the presence of the electrode, and we should have an arc discharge. If the anode were to be placed at the point *e*, we should have an arc at a minimum voltage, which might be less than the ionizing potential of the gas. It seems that the two types of discharge are really subject to the same explanation, the arc being simply the negative glow of the longer glow discharge.

This analysis suggests numerous possibilities of further test and of more quantitative treatment in particular regions of the discharge, where the experiments show that some of the factors governing the current flow become either negligible or of preponderating importance.

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