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ABNORMAL SHOT EFFECT OF IONS OF TUNGSTOUS AND TUNGSTIC OXIDE

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Abstract

Part I. The formation of positive ions of tungstous and tungstic oxide. It was found that when oxygen attacks a hot tungsten filament, positive ions are formed, and a mass spectrograph test has shown these ions to be a mixture of tungstous and tungstic oxide. The positive ion current is proportional to the pressure of the gas, as is the rate of formation of the oxide. The evaporation of an oxide layer following the pumping away of the oxygen, yields an ion current which falls away exponentially with the time. The ratio of the number of charged particles of the oxide, to the number of uncharged particles, is approximately one in twenty thousand, and this ratio does not vary greatly with the temperature of the tungsten filament.

Abnormal shot effect of the currents of positive ions. When the positive ions are drawn to a collecting electrode, in series with which there is a tuned shot circuit, an abnormal shot voltage is developed. The hypothesis is advanced that this shot voltage arises from fluctuations in the inter-electrode capacitance of the tube, caused by variations in the thickness of the electron sheath surrounding the anode as the sheath is penetrated by the positive ions. On this basis, an expression for the resulting mean square shot voltage is presented. This expression was found to be correct as regards the variation of the shot voltage with the ion current, and it has yielded reasonable values for the change in the inter-electrode capacitance.

Part II. Abnormal shot effect due to the trapping of the positive ions. When positive ions of tungstous and tungstic oxide were trapped in the minimum of potential surrounding a hot cathode, an abnormal shot voltage resulted. This abnormality was found to vary inversely with the square of the resonance frequency of the tuned shot circuit, analogously with the "flicker-effect." An expression for the mean square shot voltage has been developed, which permits the calculation of the average plate current increase due to the trapping of a single ion. The simultaneous measurement of the shot voltage and the total plate current increase has permitted the determination of the number of electrons released by each positive ion, and also the average time of trapping of the ions. From a knowledge of the trapping time, values of the electron space charge density in the minimum of potential were computed. These values were in agreement with those computed from a knowledge of the filament temperature, and the space current, and the two methods of arriving at the space charge density yielded magnitudes which varied in the same manner with the electron current through the tube.

Introduction

It is well known, particularly from the work of Kingdon and Charlton,[1] that positive ions produced at the surface of a hot filament may become trapped in the minimum of potential adjacent to the cathode surface, and will in that case cause a partial break-up of the space charge and a release of electrons to the anode. It was felt that the fluctuations of the plate current

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[1] K. H. Kingdon and E. E. Charlton, Phys. Rev. **33**, 1011 (1929).

due to this trapping process would develop an abnormal mean square shot voltage across a tuned shot circuit, and that from measurements of this voltage much information concerning the process could be obtained.

It was proposed to make use of the fact that caesium vapor becomes ionized upon contact with a hot tungsten filament, but in the course of some other work it was found that positive ions are produced when oxygen attacks a hot tungsten surface, and this source of ions was used in the experiments. Part I will be devoted to a brief discussion of this phenomenon, and of the experimental conditions governing the formation of the ions.

Before undertaking the work to be described, measurements were made of the charge carried by electrons in temperature limited currents from the filaments of several commercial vacuum tubes. These determinations were carried out with the idea of placing the apparatus in correct operating condition, use being made of the known charge carried by the electron.

As a preliminary piece of work, a determination was made of the charge of electrons produced by the ionization of argon gas. In the course of this work, large abnormalities were found to be present, as long as the electron currents were space charge limited. A detailed study of these effects was made, but space will not permit further discussion here. It will suffice to say that, when the abnormalities were eliminated, the electrons produced by the gas ionization were found to carry the accepted value of electronic charge, within the probable error of the experimental work.

The shot effect apparatus used in these determinations was of essentially the same design as that employed by Williams and Vincent,[2] in previous researches on the measurement of the charge of the electron. The experimental tubes were assembled by the writer, and varied considerably in design. The vacuum system employed was capable of maintaining a pressure of 10^{-7} mm of mercury, and was equipped with the means of introducing and mixing various gases.

PART I. THE FORMATION OF POSITIVE IONS WHEN A HOT TUNGSTEN FILAMENT IS ATTACKED BY OXYGEN GAS

It is well known, from the work of Langmuir and others, that hot tungsten is attacked by oxygen gas, with the formation of tungstic oxide. The rate of attack is proportional to the oxygen pressure, if the filament is maintained at a constant temperature. When the metallic surface is above about 1250°K, the oxide is thrown off, but when the surface temperature is below this value, the oxide forms a thick layer and the filament is very perceptibly darkened. If the coating is permitted to form on the metal, the rate of attack by the gas is decreased.

In the course of some experiments on the abnormal shot effect of currents of positive ions from pure tungsten filaments, the ions were accelerated through gases. It was found that when oxygen was admitted to the system, the positive ion current was greatly increased, and that the increase was directly due to the oxygen itself. It was immediately surmised that the ions

[2] N. H. Williams and H. B. Vincent, Phys. Rev. **28**, 1253 (1926).

were those of tungstic oxide, with the possibility of tungstous oxide being present also. Langmuir,[3] in one of his earlier papers, has shown that the attack of a tungsten surface by oxygen must take place in two steps, and he has suggested that the first may well be the formation of tungstous oxide on the metallic surface, oxygen further uniting with this compound to form the common trioxide.

As would be expected, the number of positive ions formed is very much a function of the gas pressure, the filament temperature, and the area of the tungsten surface. An idea of the magnitude of the positive ion current may be had from the fact that with a tungsten surface 1 cm^2 in area, held at a temperature of 2300°K, one may expect the saturation value of the positive ion current to be of the order of 5×10^{-5} amperes, with an oxygen pressure of 1 mm of mercury. This current is quite naturally difficult to maintain, since the gas is removed exceedingly rapidly by the filament, which is in turn eaten away. These facts have made the determination of the exact experimental relationships difficult and in some cases impossible.

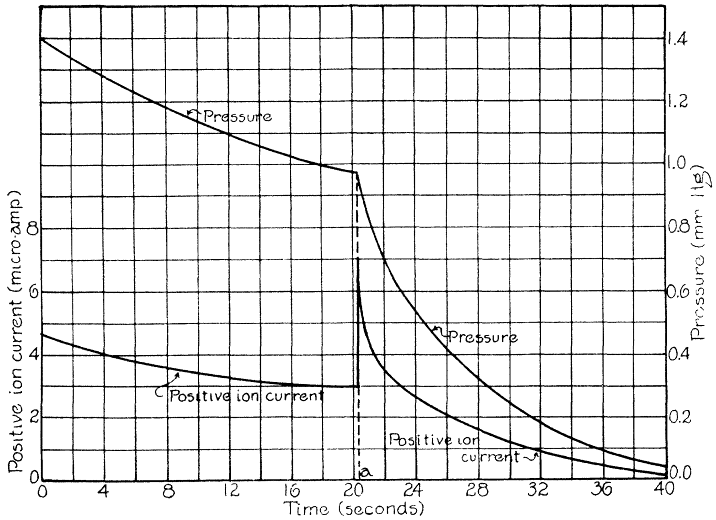

Fig. 1. Behavior of positive ion current and gas pressure, before and after evaporation of oxide layer.

As the result of experiments made with over one hundred tubes, it has been found that the rate of formation of the positive particles is directly proportional to the amount of oxygen entering into chemical combination with the tungsten to form the oxide, and it was upon this fact that the assumption as to the nature of the ions was based.

The behavior of the positive ion current and the gas pressure, with the time, is illustrated in Fig. 1. To the left of the point (*a*) on the time axis the filament temperature was so low that the oxide remained on the metallic surface. The positive ion current and the rate of decrease of gas pressure

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[3] I. Langmuir, Proc. Am. Chem. Soc. **37,** 1139 (1915).

were therefore low. At the arbitrary point (*a*) in time the filament temperature was increased sufficiently to break away the oxide layer and to prevent its re-formation. It will be noted that the positive ion current increased sharply and then fell away rapidly, as did the gas pressure, since the rate of clean-up by the fresh metallic surface was very much greater and the temperature had been increased. It will be seen from the figure that the ion current was proportional to the gas pressure, at the points beyond (*a*) in time. The rate of formation of tungstic oxide is already known to be proportional to the gas pressure, and we thus see the direct relationship between the rates of formation of the ions and of the oxide. Subsequent determinations of the variation of the ion current with the oxygen pressure have shown the direct proportionality to hold rigidly when the other experimental conditions are maintained constant.

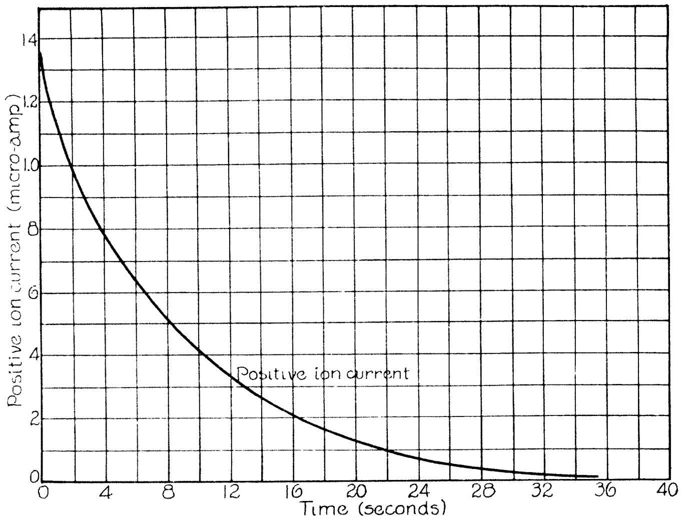

Fig. 2. Positive ion current obtained during the evaporation of an oxide coating from a tungsten filament.

It was naturally supposed that the ionization process takes place either at the moment of formation of the oxide or at the instant when the particle leaves the metallic surface, and that once the oxide is formed the oxygen gas is no longer essential. In order to test this assumption, an oxide layer was formed on a relatively cool filament, the remaining gas then pumped away and the tube walls well out-gassed. Following this treatment the filament temperature was increased sharply to a value slightly above that which would just permit the adherence of the coating. The variation of the ion current with time was then determined and the result is illustrated in Fig. 2.

From the shape of the curve of Fig. 2, it is apparent that the number of charged particules leaving the filament was proportional to the amount of oxygen resident there. No appreciable gas was given off during this breakdown process.

At the writer's request, L. P. Smith and L. Barnes, of Cornell University, lately have been so kind as to make a mass spectrograph determination of the nature of the positive ions under discussion. Their results are illustrated in Fig. 3.

It will be noted from the figure that both the singly charged dioxide and trioxide ions were present, in the approximate ratio of one to three, respectively. The presence of the dioxide ions is particularly interesting, in the light of Langmuir's conclusions as to the nature of the two-step process involved in the oxide formation.

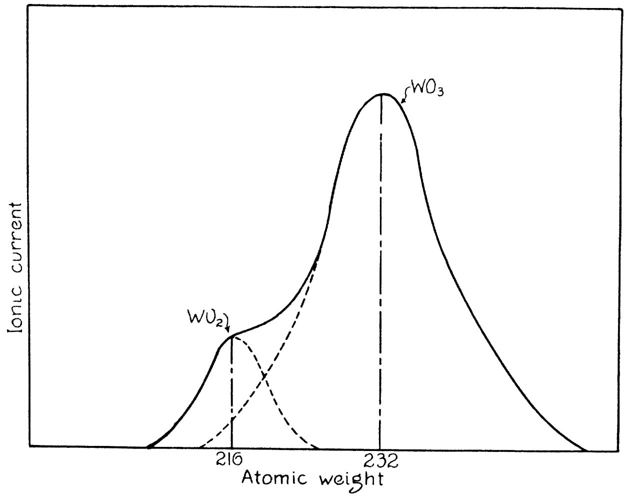

Fig. 3. Mass-spectrograph determination of the nature of the ions formed when oxygen attacks a hot tungsten filament.

THE RELATIVE NUMBER OF OXIDE PARTICLES WHICH LEAVE THE SURFACE CARRYING A CHARGE

Experiments were undertaken to determine what proportion of the particles of the oxide actually becomes charged, and how this proportion varies with the temperature of the metallic filament. In order to accomplish this, a tungsten filament was heated in an atmosphere of oxygen of a known initial pressure and volume. The total number of removed molecules of oxygen was computed from the change in pressure during the period of operation of the filament, and from this was determined the number of molecules of either WO_2 or WO_3 formed. During the heating of the filament the saturation value of the positive ion current to the cathode was measured, and the graphical integration of this curve yielded the number of ionized molecules of oxide.

The results of several representative determinations are presented in Table I. Since WO_2 is unstable chemically, the values have been computed on the basis of WO_3 alone. It is of course possible that all of the WO_2 leaving the filament was charged, and in fact it may have left the filament only by virtue of its charge.

The runs of Table I were made at different filament temperatures. The results, as regards the variation of the numbers of charged particles with the temperature, are particularly interesting. One would perhaps expect the oxide molecules to become charged more readily at the higher temperatures. This is obviously not the case, the trend being decidedly in the opposite direction toward the end of the table. It must be pointed out, however, that the smaller relative numbers of charged particles at the higher temperatures may be spurious. With the exceedingly hot filaments used in the latter runs of the table, the electron emission was high, from actual measurements, and there was a dense electron space charge surrounding the filament, which may well have brought about the removal of many of the oxide ions by recombination.

TABLE I. *Values of the ratio of the number of uncharged particles of WO_3, to the number of charged particles.*

Run	Approximate filament temperature	M/M_+
4,5	Below oxide evaporation point	14840
6	" " " "	15580
2	Just above oxide evaporation point	14940
13	" " " " "	14920
14	" " " " "	13800
10	Bright yellow heat	17560
15	" " "	17220
16	" " "	16080
17	" " "	15960
19	White heat	20600
20	" "	19940
22	" "	20560
23	" "	22600
1	Just below burn-out temperature	40400
8	" " " "	38560
9	" " " "	69200

We may conclude that, in spite of the great variation in gas pressure, filament surface condition and surface temperature from run to run, the ratio of the number of charged particles to the number of uncharged particles was of the order of one to twenty thousand and that, as regards temperature in particular, no marked variation was found.

It may be of interest to know that in experiments in which the temperature was increased uniformly until the filament burned out, the positive ion current almost invariable decreased slightly at the temperatures just below the fusion point of the tungsten. From the other results, this indicates a decrease in the rate of formation of the oxide at the highest temperatures, a result which has been predicted by Langmuir.[4]

ABNORMAL SHOT EFFECT CAUSED BY THE POSITIVE IONS OF WO_2 AND WO_3

A brief discussion of a series of determinations of the shot voltage developed by the currents of positive ions will now be presented. A tuned shot circuit was placed in the lead to the collecting electrode, and it was found that when the positive ion current traversed this circuit the resulting mean square

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[4] I. Langmuir, Proc. Am. Chem. Soc. **37**, 1139 (1915).

shot voltage was abnormal by a factor as great as one thousand, depending upon the experimental conditions.

It was apparent that the magnitude of the shot voltage was very greatly dependent upon the emission of electrons from the hot anode, entirely aside from the rate of attack by oxygen. In short, not only the positive ions were necessary to develop the abnormal shot voltage, but an electron space charge was necessary as well. This fact is clearly illustrated in the plots of Fig. 4, which are representative of many such runs.

Fig. 4 illustrates the variation of the positive ion current, the abnormal mean square shot voltage and the electron emission (determined subsequently with duplicated expermental conditions as to pressure and temperature) as functions of the time. Again at the arbitrary time (*a*) the filament was heated sufficiently to break away the oxide layer. It will be noted that before the oxide was evaporated there was a current of positive ions, as in Fig. 1, but there was no electron emission nor was there any abnormal shot voltage. With the ion currents used, the normal shot voltage was so small as to be unmeasurable. As soon as the oxide layer was removed, however, a shot voltage, abnormal by a factor of approximately 1000, appeared, whereas the positive ion current increased by only a factor of two. It is to be particularly noted that the electron emission began to build up as soon as the layer was evaporated, increasing rapidly as the oxygen was removed from the tube. A large number of determinations were made in order to check this point, and in all cases it was found that the positive ion current alone was a necessary but not sufficient condition for the abnormal shot voltage fluctuations, the electron space charge being essential also.

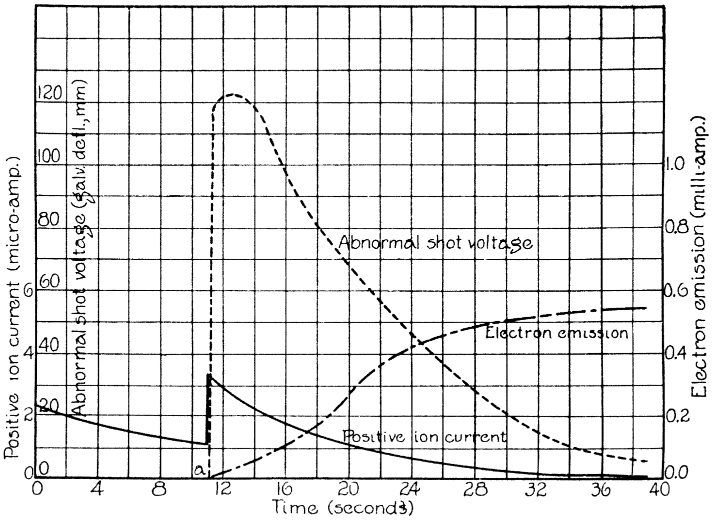

Fig. 4. Behavior of abnormal shot voltage and electron emission, following evaporation of oxide layer.

In order to explain the observed mean square shot voltage, several hypotheses were considered. It will be remembered that the field used in these experiments was a retarding one for electrons, which therefore could only leave the hot anode by virtue of their emission velocities. This resulted in an equilibrium being established between the electrons leaving the filament and those returning, the only electrons present in the tube being those in the dense sheath close to the anode surface. The only direct current traversing the shot circuit was the positive ion current, and this had been found insufficient to yield the abnormality without the presence of the electron space charge.

Of the hypotheses advanced to explain the abnormality, all but one were found to be untenable, due to the peculiar experimental conditions. The theory adopted was that the abnormality arose from fluctuations in the inter-electrode capacitance of the tube itself, caused by variations in the size of the electron space charge sheath about the hot anode as the sheath was penetrated by the massive positive particles of oxide.

On the basis of the above assumption, the writer has developed an expression for the mean square shot voltage to be found across a tuned shot circuit, in terms of the number of positive particles formed per second and the average change in the inter-electrode capacitance due to the passage of a single ion. For this expression we have:

$$\overline{E}^2 = \frac{2NK^2V^2\overline{\Delta C}^2L^2A_0{}^2A}{R^2C^2}\,. \tag{1}$$

Here, N is the number of positive ions formed per second, K a constant depending upon the time constant of the circuit, V the negative plate potential in volts, $\overline{\Delta C}$ the average change in the inter-electrode capacitance due to the passage of a single ion, L, R, C are the constants of the tuned shot circuit, A_0 the voltage amplification of the amplifier at resonance frequency and A is the area under the amplifier resonance curve, as plotted against the frequency.

By comparing the $\overline{E}^2$ of Eq. (1) with the normal shot effect $\overline{E}^2$, as developed in a tube known to yield the accepted value of the electronic charge it was found possible to measure $\overline{\Delta C}$ without a knowledge of the circuit constants or the characteristics of the amplifier.

Under the experimental conditions, Eq. (1) could only be subjected to direct test as regards the variation of $\overline{E}^2$ with N. The form of this variation was determined, and the result was entirely in accordance with the equation. Also, from measurements of $\overline{E}^2$, values of $\overline{\Delta C}$ were computed, and these were found to be of the order of 10^{-4} times the actual electrode capacitance of the tube. Since, if Eq. (1) were based upon wrong assumptions, we might just as readily obtain values for $\overline{\Delta C}$ greater than the electrode capacitance itself, the computed results are thought to lend considerable support to the assumption as to the nature of the abnormality.

PART II. ABNORMAL SHOT EFFECT DUE TO THE TRAPPING OF POSITIVE IONS IN THE MINIMUM OF POTENTIAL

Introductory. This portion of the investigation was undertaken in order to test the writer's prediction that if positive ions were to become trapped in the minimum of potential surrounding a hot cathode, an abnormal shot effect would result. One would expect the ion, when trapped, to alter the potential distribution in the space charge region, and to cause an increase in the current to the plate, which increase should persist for the duration of the stay of the ion in the region surrounding the cathode. This change in the current would not be constant, of course, but would itself fluctuate as the ion oscillated about its mean position. The phenomenon would be fundamentally different in its effect upon the shot circuit, however, from the simple passage of an ion across the tube. In the latter case the duration of the event would certainly be less than the period of the tuned shot circuit used in these experiments (10^{-5} seconds). If the ion were to become trapped, however, and if neither the loss of ions by escape from the ends of the electrodes nor the loss by recombination with electrons were excessive, the duration of the event might be expected to be greater than the period of the tuned shot circuit. As has been pointed out by W. Schottky,[5] the theoretical attack for these two cases is fundamentally different.

It was further hoped that the method of attack evolved by Schottky could be made applicable to the abnormal shot effect resulting from the trapping of the ions, and that, on this basis, a simple experimental procedure could be developed for determining the average effect of the positive ions under different conditions.

Finally, the writer wished to find a means of checking both the applicability of the Schottky theory and the quantitative experimental results to be obtained.

Preliminary experiments. In the course of the work with argon, mentioned in the Introduction, it had been found that the positive ions formed by the ionization of the gas yielded a very abnormal mean square shot voltage. This was due to the release of groups of electrons from the space charge region, as a result of the low mobility of the ions in comparison with the electron mobility. This phenomenon did not lend itself to quantitative measurements, however, since the ions were dependent upon the field for their formation, the ionization causing great instability in the tube plate characteristic and erratic readings as a consequence. Furthermore, there was no dependable method of measuring the actual number of ions formed per second.

When use was made of the ions formed by contact with oxygen with the hot tungsten filament, however, the phenomenon was fully under control. The number of ions formed was not a function of the field, but, the filament temperature being constant, was governed entirely by the oxygen pressure. This yielded separate control of the number of ions and of the space charge

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[5] W. Schottky, Phys. Rev. **28**, 74 (1926).

density, and the number of ions formed per second could be measured at once by simply reversing the potential of the collecting electrode.

With the use of oxygen, and when the electron currents were space charge limited, it was found that the mean square shot voltage was abnormal by a factor of from 100 to 1000, depending upon the density of the space charge. The abnormality disappeared as soon as the electron currents were temperature limited. It remained to be determined whether or not the large shot voltage was due to the trapping of the ions, giving a result of the same nature as the "flicker effect."

Schottky[6] has shown that, if the abnormal shot effect is caused by a primary event whose duration is greater than the period of the tuned shot circuit used, we would expect the shot voltage to vary inversely as the square of the resonance frequency of the tuned circuit. The particular case for which Schottky's theory was developed was the shot effect found experimentally by J. B. Johnson,[7] and explained on the basis of fluctuations in emission caused by the temporary residence of foreign molecules on the emitting surface. This phenomenon followed the inverse square variation with the frequency of the tuned shot circuit.

Determinations were made of the trend with frequency of the abnormality in argon, and of the abnormality resulting from the positive ions of tungstous and tungstic oxide. In the former case, no definite frequency variation was found in the region from 100 to 250 kilocycles. In the latter case, however, the shot voltage was found to exhibit, within a few percent, the inverse square frequency variation. This at once classified the abnormality in oxygen as a phenomenon of the nature of the "flicker effect," with a primary event lasting longer than the period of the tuned shot circuit, and indicated that the cause of the abnormality was undoubtedly the trapping of the positive ions in the region of the minimum of potential, rather than the simple passage of an ion through the space charge region.

Theory. If we let γ be the average plate current increase due to the trapping of a single positive ion, we find that it is possible to obtain an expression for γ in terms of quantities easily measured experimentally. It may be pointed out that for the moment we are not interested in the factors limiting the duration of this average current increase, but only in the fact that, as was determined by the experimental frequency trend, the duration of the increase is substantially greater than the period of the tuned shot circuit.

The shot circuit consists of a tuned impedance in the plate lead of a two electrode tube and, in addition to the steady average value of the plate current, we have flowing through it a fluctuation current (due to electrons released from the space charge region) which may be written in terms of its Fourier components as follows:

$$j = \sum_{k=1}^{\infty} A_k \cos \omega_k t + \sum_{k=1}^{\infty} B_k \sin \omega_k t = \sum_{k=1}^{\infty} C_k \sin (\omega_k t + \Phi_k) \tag{2}$$

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[6] W. Schottky, Phys. Rev. **28**, 74 (1926).

[7] J. B. Johnson, Phys. Rev. **26**, (July, 1925).

where A_k, B_k, and C_k are partial current amplitudes and ω_k is $2\pi x$ the frequency of the kth component.

Of course:

$$\left.\begin{aligned} \overline{A_k^2} + \overline{B_k^2} &= C_k^2 \\ \overline{A_k^2} &= \overline{B_k^2} \end{aligned}\right\} \tag{3}$$

and:

Schottky[8] has evaluated these coefficients in his treatment of the "flicker effect," with the only difference that the fluctuations in the electron current originated at the cathode surface, rather than at the potential minimum, as in our case. Schottky obtained the result:

$$\overline{A_k^2} = \overline{B_k^2} = \frac{2}{T}\cdot\frac{\beta^2\gamma^2\alpha}{\alpha^2 + \omega_k^2} = \frac{2}{T}\cdot\frac{n\gamma^2}{\alpha^2 + \omega_k^2} \tag{4}$$

(since $\overline{\beta^2} = N_0$ from probability considerations, and $N_0\alpha = n$.)

In this expression T is a time of observation, α the reciprocal of the time of trapping of an ion, N_0 the average number of ions in the space charge region at any instant, β the momentary deviation from this average, n the number of ions formed per second and ω_k is $2\pi x$ the frequency of the kth component of the fluctuation current.

We therefore have:

$$\overline{C_k^2} = \frac{4}{T}\cdot\frac{n\gamma^2}{\alpha^2 + \omega_k^2}\,\cdot \tag{5}$$

If a fluctuation current j is passed through a tuned shot circuit, and the resulting voltage fluctuations across the terminals of the tuned shot circuit are amplified, Williams and Vincent[9] have shown that the mean square shot voltage is given by:

$$\overline{E^2} = \sum_k \overline{E_k^2} = \frac{L^2A_0^2}{2R^2C^2}\sum_{k=1}^{\infty} C_k^2\Phi(x) \tag{6}$$

where A_0 is the voltage amplification of the amplifier at resonance frequency and $\Phi(x)$ is the curve obtained by plotting the relative power output at different frequencies against $x = \omega_k/\omega_0$.

If $dx = 2\pi/\omega_0 T$ be substituted in (6), together with C_k^2 from Eq. (5), we obtain:

$$\overline{E^2} = \frac{1}{\pi}\cdot\frac{L^2A_0^2}{R^2C^2\omega_0}\int_0^{\infty}\frac{n\gamma^2}{x^2 + \alpha^2/\omega_0^2}\Phi(x)dx. \tag{7}$$

The integrand of Eq. (7) may be considerably simplified if $\alpha << \omega_0$. In the experimental case, α will be found to be of the order of 10^4 and ω_0 was approximately 10^6. Therefore α^2/ω_0^2 was approximately 10^{-4} and could be neglected in comparison with x^2, which was very nearly unity.

Eq. (7) then becomes:

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[8] References 5 and 6.

[9] N. H. Williams and H. B. Vincent, Phys. Rev. **28**, 1253 (1926).

$$\overline{E^2} = \frac{n\gamma^2L^2A_0^2}{R^2C^2\omega_0}\int_0^\infty \frac{\Phi(x)}{x^2}dx. \tag{8}$$

A further simplification may also be carried out. If we write $1/z$ for x in the integrand of (8), we obtain:

$$\overline{E^2} = \frac{n\gamma^2L^2A_0^2}{R^2C^2\omega_0}\int_0^\infty \Phi\left(\frac{1}{z}\right)dz. \tag{9}$$

But it may be shown that if the amplifier resonance curve is sharp and symmetrical, as is true in the experimental case, we may write:

$$z = 1/z$$

with an error of only about 0.1%.

Thus:

$$\Phi\left(\frac{1}{z}\right) \backsimeq \Phi(z)$$

and (9) becomes:

$$\overline{E^2} = \frac{n\gamma^2L^2A_0^2}{R^2C^2\omega_0}\int_0^\infty \Phi(x)dx \tag{10}$$

This equation may be written in terms of the frequency, since $x=\omega/\omega_0$ and $\nu=\omega/2\pi$. We thus obtain:

$$\overline{E^2} = \frac{2n\gamma^2L^2A_0^2}{R^2C^2\omega_0^2}\int_0^\infty \Psi(\nu)d\nu. \tag{11}$$

But $\int_0^\infty\Psi(\nu)d\nu$ is the area under the curve obtained by plotting the relative amplifier out-put voltage, for constant input, against the frequency, and may be called A.

Thus:

$$\overline{E^2} = \frac{2n\gamma^2L^2A_0^2A}{R^2C^2\omega_0^2}\cdot \tag{12}$$

Circuit constants and the necessity of plotting the resonance curve may be eliminated by comparing this $\overline{E^2}$ with the normal shot effect $\overline{E^2}$ obtained from a comparison tube known to yield the accepted value of electronic charge, and in which the electron current has been adjusted to give the same $\overline{E^2}$ as the abnormal effect.

Thus:

$$\frac{2n\gamma^2L^2A_0^2A}{R^2C^2\omega_0^2} = \frac{2i_0\epsilon L^2A_0^2A}{R^2C^2}\cdot^{10} \tag{13}$$

In the second member of this equation, ϵ is the electronic charge and i_0 the electron current necessary to yield the desired value of $\overline{E^2}$.

Simplifying, we obtain:

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[10] N. H. Williams and H. B. Vincent, Phys. Rev. **28,** 1253 (1926).

$$\gamma = \omega_0\left(\frac{i_0\epsilon}{n}\right)^{1/2} \tag{14}$$

which is the expression for the average plate current increase due to the trapping of a single positive ion. From a consideration of the right hand side of the equation, it will be seen that we now have a means of determining. experimentally the size of the primary event of the phenomenon in question.

In the course of the experimental work it was found, as would be expected, that during the attack ofthe filament by oxygen the shape of the plate current characteristic of the tube was altered. The break-up of the space charge by the positive ions resulted in an increase in current in the range of plate potentials wherein the current was limited by space charge. The effect of this may be seen in Fig. 5. The method of taking this plate current characteristic will be discussed in a subsequent paragraph.

If we let Δi_P be the increase in plate current, at any one plate potential, due to the action of all of the ions, and let τ be the average time of life of an ion in the minimum of potential, we see that $\gamma\tau$ is the average charge released by one ion, and $n\gamma\tau$ is the charge released per second, which is precisely the total change in the current.

Therefore:

$$\Delta i_p = n\gamma\tau. \tag{15}$$

It may now be seen that, if n is known from the saturation value of the positive ion current with reversed field, Δi_P known by direct measurement, and γ computed from the shot effect determinations, substituted in Eq. (14), we have a means of computing τ, the average time of life of the ions in the minimum of potential.

In addition, it is of interest to determine a value of the number of electrons released by each positive ion. This may be had by dividing Δi_P by the saturation positive ion current under reversed fields.

It seemed possible that, from the value of τ, the magnitude of the space charge density in the minimum of potential might be computed and checked against magnitudes computed from a knowledge of the filament temperature and the space current. It was thought that this might offer a means of verifying our theory, in particular the applicability of the "flicker-effect" Fourier coefficients to this experimental case.

The writer is not aware of any exact formula connecting τ and the electron space charge density, but Kingdon and Charlton[11] have given the approximate relation:

$$\rho = \frac{\left(\dfrac{2\pi m}{KT_f}\right)^{1/2}}{4\pi b^2\tau} \tag{16}$$

where m is the electron mass, T_f the filament temperature, and b is a parameter having the value 3.25×10^{-7} for a temperature of 1700°K.

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[11] K. H. Kingdon and E. E. Charlton, Phys. Rev. **33**, 1012 (1929).

It is obvious that, in making use of this equation, we are assuming that the life of the positive ions is limited solely by recombination with electrons. The other principal factor which might limit the time of existence of the ions in the minimum of potential is escape from the ends of the electrodes. In order to test for this effect, a special tube was constructed, having shields over the ends of the plates which could be so charged as to repel the ions back into the region about the filament. It was found that the effect of loss by escape was not appreciable with the low gas pressures at which the latter work was carried out. The region of pressure in which it was necessary to work will be discussed in a following paragraph.

The method of computing the space charge density in the minimum of potential, from a knowledge of the filament temperature and the space current, is too well known to require description. We need only refer the reader to the papers of Langmuir[12] and Kingdon and Charlton.[13]

In the present work, we could not hope to check very closely the values computed by the last mentioned method, since Eq. (16) is not exact. However, since the rate of recombination must certainly vary directly with the space charge density, the variation:

$$\rho \sim \frac{1}{\tau} \tag{17}$$

may be expected to be true. In short, if our theory is correct, we would expect the values of ρ computed from the experimental results to behave, with some variable such as the space current, in the same manner as the values of ρ computed from purely theoretical considerations. If our theory were incorrect, this would certainly be most unlikely. This, then, yielded a means of testing the ideas outlined in this section.

Experimental Procedure. In the final experimental runs, made to test the foregoing theory, the oxygen pressure was maintained constant by pumping air through a slow-leak stop-cock and past the hot filament. Control experiments showed that the nitrogen and water vapor from the air were entirely inert and acted in no way to invalidate the work.

Determinations of the variation of the positive ion current with the oxygen pressure demonstrated a direct proportionality, from the lowest measureable pressures until the chemical action was so rapid as materially to decrease the surface of the filament during a run. At the higher gas pressures the number of positive ions formed per second was computed from direct measurement of the positive ion current under reversed field. At the low oxygen pressures, where the ion current was unmeasurable with a microammeter, readings of the current were taken at the higher pressures and the values extrapolated.

Before admitting oxygen to the tube, the vacuum plate current characteristic was taken. (See Fig. 5.) The utmost care was necessary in the determination of this curve, as the amount of oxygen given out by the

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[12] I. Langmuir, Phys. Rev. **21**, 419 (1926).

[13] K. H. Kingdon and E. E. Charlton, Phys. Rev. **33**, 1011 (1929).

walls and electrodes, even after considerable baking and out-gassing, was sufficient to raise the characteristic curve in the region of space charge limited currents. This led to erroneous values of Δi_P.

Δi_P would be expected to vary linearly with the gas pressure, from Eq. (5), and a number of experiments were carried out to determine the range of gas pressures in which this was true. It was found that, with the tubes used, the linear variation held only up to pressures of the order of 10^{-4} mm of mercury. At higher gas pressures, Δi_P exhibited a saturation, no doubt partially due to the increased effect of the escape of the ions from the ends of the electrodes. At the same pressure, ρ_m also began to fall away rapidly from the values computed by Langmuir's equations. For these reasons the pressures used in the final experiments were of the order of 10^{-4} mm of mercury or less.

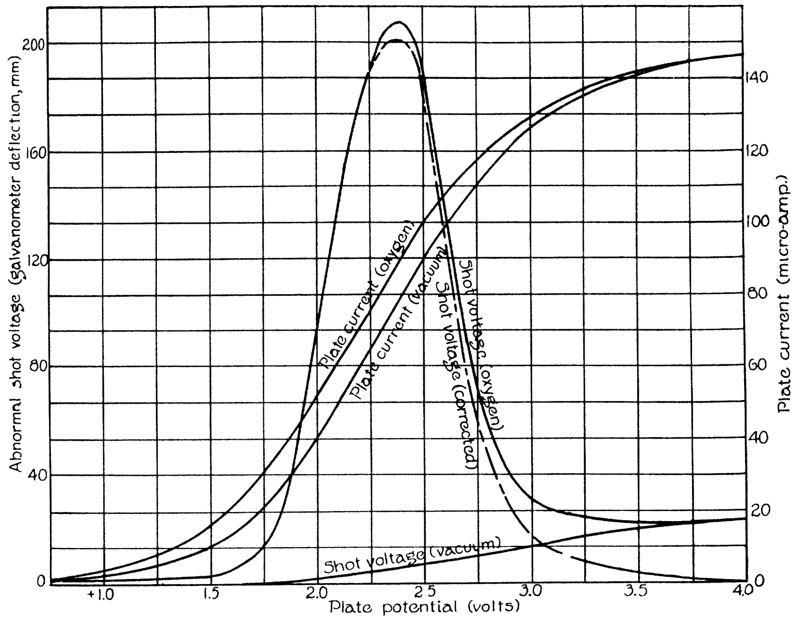

Fig. 5. Plate currents and mean square shot voltages as functions of the plate potential, in a vacuum and in oxygen.

Following the taking of the plate characteristic curve in a vacuum, the oxygen pressure was adjusted to the desired value and a determination of n made. The plate current characteristic of the tube was re-taken, together with the corresponding values of the abnormal mean square shot voltage. These latter were determined by means of the standard shot circuit and an amplifier which had been calibrated in terms of electron currents in a tube known to yield the accepted value of the electronic charge.

The values of γ, τ and ρ_m were computed from equations (14), (15) and (16), respectively. ρ_m was also computed from the equations of Langmuir and Kingdon and Charlton, and these latter space charge densities were compared with those obtained from the experimental results.

Results. Only one typical experimental run will be presented here. Fig. 5 illustrates the variation of the plate current in a vacuum and in oxygen, with the positive plate potential, and also the variation of the mean square shot voltage in both cases, with the same independent variable. The actual computations of γ, τ and ρ_m were carried out from the dotted curve. This last was obtained by first adjusting the vacuum shot voltage curve for the fact that the actual plate currents were higher in the second case, and then subtracting the result from the shot voltage curve obtained in oxygen.

TABLE II. *Values of η, γ, τ and ρ_m, computed from the experimental results illustrated in Fig. 5.*

E_p (volts)	η	γ (amperes)	τ (sec.)	ρ_m (experimental)	ρ_m (theoretical)
1.50	1.24×10^5	0.925×10^{-10}	2.13×10^{-4}	0.55×10^9	0.42×10^9
1.55	1.36	1.18	1.850	.637	
1.60	1.46	1.44	1.610	.728	
1.65	1.58	1.85	1.360	.861	
1.70	1.68	2.09	1.270	.920	
1.75	1.80	2.72	1.050	1.118	.790
1.80	1.94	3.27	.94	1.241	
1.85	2.06	3.94	.83	1.410	
1.90	2.22	4.92	.72	1.635	
2.00	2.38	6.98	.57	2.041	1.390
2.05	2.52	7.85	.52	2.230	
2.10	2.60	8.71	.45	2.630	
2.15	2.44	9.22	.41	2.820	
2.20	2.40	9.61	.38	3.080	
2.25	2.20	10.08	.35	3.360	2.130
2.30	2.14	10.32	.33	3.550	
2.35	2.10	10.52	.32	3.690	
2.40	2.06	10.31	.31	3.750	
2.45	2.00	10.08	.308	3.800	
2.50	1.80	10.00	.284	4.110	2.960
2.55	1.70	9.24	.293	3.990	
2.60	1.60	8.38	.303	3.860	
2.65	1.40	7.65	.291	4.02	
2.70	1.10	6.54	.267	4.38	
2.75	.90	5.65	.254	4.60	3.740
2.80	.80	4.95	.257	4.55	
2.85	.60	4.50	.212	5.50	
2.90	.50	3.96	.200	5.84	
2.95	.44	3.42	.205	5.70	
3.00	.40	2.92	.218	5.36	4.470
3.05	.34	2.83	.191	6.12	
3.10	.20	2.63	.121	9.65	
3.15	.16	2.42	.104	—	
3.20	.10	2.31	.069	—	
3.25	.04	2.06	.031	—	—

The oxygen pressure chosen for this particular determination was 3.75×10^{-5} mm of mercury, which was well within the range of the linear variation of Δi_P with the gas pressure.

In Table II we have listed, for different plate potentials, the computed values of η (the average number of electrons released by each positive ion), γ, τ, and the experimentally determined values of ρ_m, which are the magnitudes of the electron space charge density in the potential minimum, computed from the experimental results. In the last column are listed the values of ρ_m computed from the equations of Langmuir and Kingdon and Charlton. It will be noted that both η and γ reach a maximum, but not at the same plate potential, since η is proportional to the product of τ and γ. The values of τ are seen to decrease throughout the table, since the space charge (and hence also the amount of recombination with electrons) is decreasing. It will be noted that the values of τ are substantially greater than the period of the tuned shot circuit, which was in this case approximately 4×10^{-6} seconds.

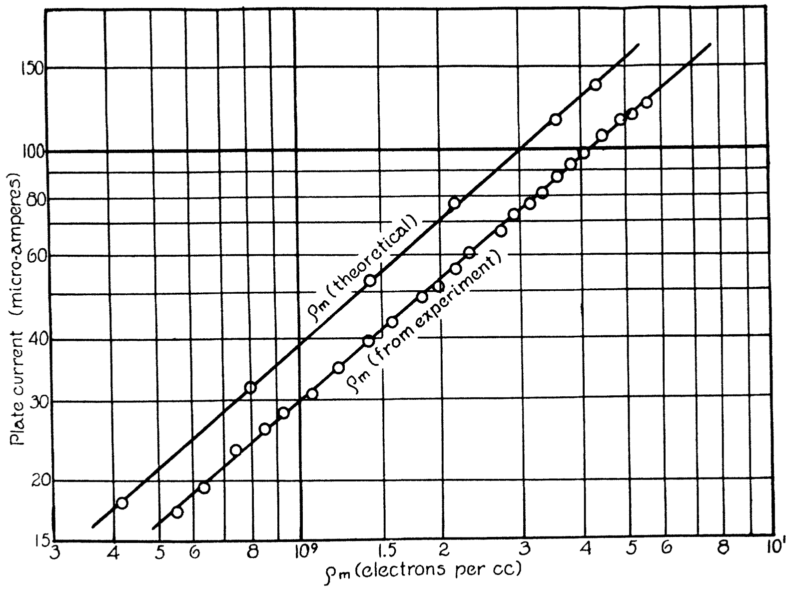

Fig. 6. Logarithmic plots of ρ_m, computed by the two different methods, against the logarithm of the space current.

In Fig. 6 we have the two different sets of values of ρ_m plotted against the space current, to logarithmic scales. As indicated in the last two columns of Table II, the values of ρ_m computed from the experimental results, agree with the values computed from purely theoretical considerations, within the probable error of the experiments and of Eq. (16). Fig. 6 shows that the two values of ρ_m varied in almost an identical manner with the space current, in spite of the fact that the experimentally determined magnitudes continue across the maxima of both the shot voltage and of Δi_P. (Fig. 5)

Summary and Conclusions

In the first part of this report, the formation of charged particles of tungstous and tungstic oxide was described. As far as the writer is aware, this has not been reported in the literature, and it is thought that the results will be of interest to those working with the general problem of emission from various types of filaments.

In Part I we briefly described the abnormal shot effect resulting when the positive ions formed at the surface of the filament were accelerated through the dense electron space charge region surrounding the hot tungsten surface. This abnormality is interesting in that the fluctuations were not those of the direct current traversing the tuned shot circuit, since the large shot voltage was absolutely dependent upon the presence of the electron space charge. On the hypothesis that the primary event in the process is the fluctuation in the inter-electrode capacitance of the tube itself, due to variations in the thickness of the dense electron sheath, we were able to develop an expression for the mean square shot voltage in terms of the change in capacitance. Computations of ΔC from the experimental results yielded values which were entirely consistent with the actual electrode capacitance of the tube.

In Part II a study was made of the abnormal shot effect resulting from the trapping of the positive ions in the potential minimum surrounding the hot cathode. Tests of the frequency trend demonstrated that the phenomenon was of the nature of the "flicker-effect," the primary event persisting for a time longer than the period of the tuned shot circuit. From a consideration of the effect of the fluctuations upon the tuned circuit, an expression was developed for the experimental determination of the average increase in plate current caused by the trapping of a single ion. In addition, a means was found for determining the average time of life of an ion in the potential minimum, and the average number of electrons released by each ion.

As a means of checking the applicability of the theory, the values of the electron space charge density in the potential minimum were computed, and compared with the values obtained from a knowledge of the filament temperature and the space currents. The two sets of magnitudes of ρ_m were in agreement within the probable error of the experimental results and the equations used, and they were found to vary in exactly the same manner with the space current itself, throughout the range of plate potentials in which the currents were space charge limited. It is considered that these results lend strong support to the theory outlined in Part II.

As regards the technical aspects of the problem, it is obvious that the abnormal shot effects dealt with, and those mentioned in the introduction, are contributory factors to the noise in commercial vacuum tubes. The technique of abnormal shot effect should prove to be a powerful tool for the investigation of tube noise, and for the determination of the means of its elimination.

In conclusion, the writer wishes to express his indebtedness to Professor N. H. Williams, of this Department, under whose direction the work was carried out.