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PHENOMENA IN OXIDE COATED FILAMENTS

By Joseph A. Becker
Bell Telephone Laboratories, 463 West Street, New York, N. Y.

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Abstract

A theory of the changes in activity in oxide coated filaments is proposed. From a comparison of the behavior of these filaments and filaments with composite surfaces such as thorium on tungsten, caesium on tungsten, and caesium on oxygen on tungsten it appears probable that oxide coated filaments owe their high activity to adsorbed metallic barium. The changes in emission from a coated filament produced by changes in plate potential and by currents sent into or drawn from it, are ascribed to electrolysis of the oxide. When electrons are sent into a coated filament barium is deposited on the surface and the activity increases until an optimum is reached beyond which the activity decreases. When current is drawn from the oxide, oxygen is deposited on the surface. If the oxygen is beneath the adsorbed barium, it increases the activity; if it is above the barium, it decreases the activity. Both barium and oxygen diffuse readily from the surface into the oxide and vice versa. This theory is tested, confirmed, and extended by numerous experiments.

An experimental technique is employed by which relative rates of evaporation of small amounts of electropositive and electronegative materials can be determined with considerable precision. The same technique might be useful in a number of similar investigations. Metallic barium or oxygen which evaporate from a coated filament are allowed to deposit on one side of a flat tungsten ribbon whose thermionic activity is followed. When the plausible assumption is made that an optimum activity is obtained when the tungsten is covered with a single layer of electropositive material, the relative rates of evaporation can be converted to absolute rates. This technique is also employed to determine the factors which control the evaporation of oxygen from a coated filament.

Experimental results.—(1) *Metallic barium evaporates* from a well broken down coated filament provided that the temperature is not too high and that no appreciable currents are drawn. (2) *Oxygen evaporates* if an emission limited current is drawn and the temperature is high enough. (3) *Metallic barium* which is deposited on the surface of the oxide either by electrolysis or by evaporation from an outside source, *produces changes in activity* of the same sort as are produced by barium on tungsten. (4) *Barium or oxygen diffuse* readily to and from the surface of the oxide (5) *Oxygen* brought to the surface of the oxide by drawing current from it, *increases* the *activity* under some circumstances *and decreases it* under others. (6) *Most of the current through the oxide is carried by electrons* but a small part is carried by ions; the ratio depends upon the temperature, the composition of the oxide, and the plate potential. It appears that *the conductivity of the oxide does not obey Ohm's law* and that some of the conductivity is due to a diffusion current which may flow against an opposing field. (7) *The complex time changes* that occur in coated filaments *are described* in a systematic manner.

Introduction

A METALLIC filament which is covered with one or more of the oxides of calcium, strontium, or barium is called an oxide coated filament. It has long been known that such filaments when properly treated are exceedingly good emitters of electrons. They have found considerable use in thermionic vacuum tubes and in scientific investigations. The object of this paper is to present a scientific description of some of the processes occurring in some oxide coated filaments and to propose a comprehensive theory to account for these processes.

There are two types of oxide coated filaments: those in which some or all of the oxides have been made to combine chemically with the metallic core of the filament, and those in which the oxides are uncombined. The latter appear pure white. In the combined filaments, the chemical compounds are decomposed when the tube is pumped. This leaves a finely dispersed metal mixed with the oxides and gives the filaments a grayish appearance. A method of preparation of combined filaments is described by Arnold.[1] The preparation of uncombined filaments is described by Schottky, Rothe and Simon, Volume 13, Part 2 of the Wien-Harms "Handbuch der Experimental-physik" pp. 215 and 305.[2] The reader will find a good discussion of published articles on oxide coated filaments in this same volume. The author's experience with barium oxide+strontium oxide combined filaments has been more extensive than with others.

In either type of filament, but particularly in combined filaments, it is found that the thermionic activity is greatly enhanced by what has been variously termed the activation, formation, or breakdown process. We shall call it the breakdown process. This process consists in glowing the oxide coated platinum filament at about 1500°K for several minutes; a rather high positive potential gradient is then applied to the filament for something like two to thirty minutes. During this time the emission from the filament increases greatly. When it attains rather large values such as 0.1 to 1.0 amps. per cm^2, the applied field and the filament temperature are so adjusted that the current is just limited by space charge. The detailed procedure to be followed for any particular filament constitutes an art and is beyond the scope of this article. The processes that go on during this time will be discussed below. The behavior of the filament before and after breakdown is considerably different.

Throughout this article we shall frequently use the term "activity" of the filament. As a measure of the activity we shall take the emission current at one particular temperature or at a series of temperatures. These temperatures will all be low and the plate potential will have a small constant value in order that the currents may remain essentially constant during the time required to determine the activity.

One of the outstanding characteristics of a coated filament is its complex behavior. For example, coated filaments show changes in activity with time following upon or accompanying (1) changes in temperature, (2) changes in plate potential and (3) current sent into or drawn from the filament. While all coated filaments show time changes with these three variables, the magnitude and even the direction of the change in activity depends greatly on the chemical and physical composition of the oxide as well as on the previous

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[1] H. D. Arnold, Phys. Rev. **16**, 70 (1920).

[2] The title to this volume is "Glühelektroden und Technische Elektronenröhren "

treatment both immediate and remote. From this it is apparent that the coated filament is an extremely complex system. In our attempt to discover the processes going on in this complex system, we have found it convenient to be guided by a tentative hypothesis or unifying picture, and the reader may find it helpful to consider this hypothesis.

HYPOTHESIS OR THEORY OF THE ACTION IN COATED FILAMENTS

In constructing such a hypothesis it is desirable to consider simpler types of filaments and to compare them with oxide coated filaments. The simplest kind of filament is one having an atomically clean and homogeneous surface such as clean tungsten, tantalum, or molybdenum. For any of these filaments the emission is determined solely by the temperature and plate potential; it is independent of the time of treatment at any previous temperatures, plate potentials or emission currents.

A somewhat more complex type of filament is illustrated by thoriated tungsten,[3] caesium on tungsten,[4,5] or barium on tungsten. These filaments have composite surfaces: the tungsten surface is more or less covered by a partial layer, a complete layer, or more than one atom layer of a foreign element. The activity, or emission at a testing temperature and fixed plate potential, now depends on the kind of foreign element and on θ, the fraction of the surface covered with it. Figure 1 shows the logarithm of the emission for barium on tungsten at 1100°K as a function of θ. Note that the activity is increased by a factor of about 10^{11} by a complete layer of barium. Since the amount of barium on the surface can be changed by heating the filament, it follows that in this case the activity can be greatly modified by a temperature treatment. On the other hand, experiment shows that the activity and θ are not affected by the plate potential or by the electron current sent into or drawn from the filament.

A still more complex filament is one with a doubly composite surface such as caesium and oxygen on tungsten. In this case experiment apparently shows that the activity depends upon (1) the number of caesium atoms per cm^2, (2) the number of oxygen atoms per cm^2, and (3) the relative position of the caesium and the oxygen. The activity increases with the amount of caesium until the surface is covered with a monatomic caesium layer; then it decreases as the second layer is formed. If we start with a monatomic layer of caesium and add increasing amounts of oxygen to the hot filament, the activity is increased even more, provided the amount of oxygen is small; as more and more oxygen is added, the activity comes to a maximum and then decreases. Temperature treatments change the concentration of caesium and of oxygen and consequently they also change the activity. Temperature may also affect the activity by changing the relative position of the caesium and oxygen.

That the activity depends on whether the caesium is on top of the oxygen or the oxygen on top of the caesium, is not yet established by direct experi-

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[3] Langmuir, Phys. Rev. **22,** 357 (1923).

[4] Langmuir and Kingdon, Proc. Roy. Soc. **107A,** 61 (1925).

[5] Becker, Phys. Rev. **28,** 341 (1926).

ments. This view is based on the author's interpretation of temperature changes in the analogous case of barium and oxygen on tungsten and on the theory of the cause of the increase in activity for composite surfaces.* On this view,** if oxygen is deposited on top of a monatomic layer of caesium on tungsten and stays there, the activity should decrease; but if thermal agitation causes the oxygen to settle down between the tungsten and the caesium, the activity should increase. Such surface rearrangements take place apparently at temperatures lower than those necessary to produce other surface changes such as surface migration, diffusion inward, or evaporation. Temperature treatments can thus change the activity by changing the amount of caesium, amount of oxygen, or their relative positions. But even with this complex filament, the activity is independent of plate potential and the amount of current sent into or taken out of the filament.

Since coated filaments show changes in activity with temperature treatments in much the same way as do filaments with composite surfaces, it is quite natural to assume that coated filaments also have a composite surface of presumably metallic barium† on the oxide. This view is supported by another striking similarity between oxide coated filaments and filaments which are known to have composite surfaces. In both cases the emission current increases quite appreciably as the plate potential is increased more and more, while the emission current from an atomically clean surface saturates quite well.[6+]

Because of these two similarities, the author in private laboratory reports proposed the hypothesis that the enhanced activity of oxide coated filaments is due to metallic barium on the surface of barium oxide. Numerous experiments made in this laboratory have fully confirmed this hypothesis. The same or a similar hypothesis was proposed by Koller[7] in 1925, Rothe[8] in 1926, Espe[9] in 1927, and Detels[10] in 1927.

This hypothesis takes into account the similarities in coated and composite surface filaments but it fails to take into account the dissimilarities. It has been emphasized above that the activity of a coated filament is changed by changes in plate potential and by the current sent into or drawn from it, while the activity of other forms of composite surface filaments is not. It follows that an additional hypothesis must be made for

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* See 15 below.

** This view was held by Mr. Ryde of the G. E. Laboratory at Wembley, England in 1928. He was kind enough to discuss the matter with the author on his visit to America.

† Throughout this article barium will be used as representative of the group of alkaline earths. It is to be understood that calcium and strontium act qualitatively like barium.

[6] See "On Electrical Fields near Metallic Surfaces" by Becker and Mueller, Phys. Rev. **31,** 431 (1928).

[+] In oxide coated filaments poor saturation may sometimes be produced by additional causes such as heating effects in the oxide or localized space charges.

[7] Koller, Phys. Rev. **25,** 671 (1925).

[8] Rothe, Zeits. f. Physik **36,** 737 (1926).

[9] Espe, Wissenschaftliche Veröffentlichungen aus dem Siemens Konzern, **5,** 29 and 46 (1927).

[10] Detels, Jahrbuch der Drahtlosen Telegraphie und Telephonie **30,** 10 and 52 (1927.

coated filaments. Electrolysis of the oxides naturally suggests itself since it has been known for many years that heated salts and in particular some oxides are electrolized. This was shown by the work of Bose,[11] Horton,[12] and Spanner.[13] From what is known of the conductivity of oxides, it may safely be postulated that the current perpendicular to the surface of the oxide may be carried partly by electrons and partly by ions, presumably of barium and oxygen.

This hypothesis too was proposed by the author in private laboratory reports. It had previously been held by Fredenhagen[14] in 1913, who believed, however, that the emission of electrons was caused by chemical recombination of barium and oxygen. The electrolytic hypothesis was also held by Rothe,[8] Espe,[9] and Detels.[10] They and others showed that an oxide coated filament which has been heated to a high temperature for a considerable time does not give off appreciable quantities of gas if no current is drawn from it, but that considerable gas is given off when curernt is subsequently drawn. Detels[10] showed that this gas was oxygen by collecting it in a Geissler tube and showing that its spectrum was identical with that of a similar tube filled with pure oxygen. J. E. Harris in these laboratories first showed that if large currents are drawn from a barium oxide+strontium oxide coated filament, barium and strontium are present in the core, while if a similar filament is glowed even more severely but without drawing currents, no barium or strontium are found in the core. It is thus clearly established by numerous and varied experiments that some electrolysis takes place in oxide coated filaments and that the products are the ones to be expected. It is proper, therefore, to attempt to account for the observed changes in activity with drawing current or sending current into the filament on the basis of the electrolytic theory.

On the electrolytic theory, if electrons are sent into a coated filament from another source, barium is deposited on the outer surface of the oxide while oxygen is deposited on the interface between the core and the coating. Since thermionic emission depends on surface conditions and not on the conditions many layers beneath the surface, the barium should directly and immediately affect the activity while the oxygen should not do so. If barium on barium oxide produces the same effects as does barium on the tungsten, the activity should increase, pass through an optimum and then decrease as more barium is deposited on the surface. Experiments to be described below show that this is precisely what happens. These experiments will also be used to determine quantitatively the factors that determine the amount of electrolysis.

If, on the other hand, electrons are drawn from a coated filament, barium is deposited on the core-oxide interface and oxygen on the outer surface. The barium should not affect the activity directly and immediately but may

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[11] Bose, Ann. d. Physik **9,** 164 (1902).

[12] Horton, Phil. Mag. **11,** 505 (1906).

[13] Spanner, Ann. d. Physik **75,** 609 (1924).

[14] Fredenhagen, Leipziger Berichte **65,** 42 (1913).

do so if it subsequently diffuses to the oxide surface. The oxygen, however, should affect the activity directly and immediately. From analogy with caesium and oxygen on tungsten discussed above, the change in activity due to additional oxygen should depend on the amount of barium, the amount of oxygen, and also on the position of the oxygen relative to any surface layers of barium or barium-oxide. The experiments described below fulfill this expectation. They show that when current is drawn from a coated filament, the activity sometimes decreases, while at other times it increases to a maximum and then decreases. Which of these behaviors is exhibited depends upon the degree of breakdown of the filament, the temperature, and the plate potential.

Another supplementary hypothesis is required to account for the complex behavior in coated filaments. It is to be expected that the barium and oxygen which are produced by electrolysis will diffuse into the oxide and from the oxide to the outer surface where they produce their effect on the activity. On account of the open or spongy structure of the oxides on these filaments, we should expect diffusion to take place very readily since it has been shown that surface migration of adsorbed atoms takes place at temperatures at which evaporation is negligible.[15] At temperatures near 1000°K there should be a continuous interchange of barium and oxygen atoms between the surface and the interior of the oxide.

The various phases of the proposed hypothesis have been thoroughly tested, confirmed, and extended by the experiments which are described below. For this reason it seems proper to speak of the theory rather than the hypothesis of oxide coated filaments.

Experimental Tubes

Most of the experiments were performed with two tubes designated by 12-J and 89-B. Figure 2 shows the plate and filament assembly of tube 12-J. The plates were made of preglowed nickel. The dimensions are given in the figure. Usually only the current to the center plate was measured; the end plates served as guard plates. F_1 and F_3 are oxide coated filaments. The core consisted of a 95 percent platinum, 5 percent nickel alloy in the form of a ribbon $10.2\times0.030\times0.0054$ cm. They were coated with about 20,000 molecular layers of barium oxide and strontium oxide and were flashed at 1000°K in air to form some barium and strontium platinates and nickelites. F_1 was broken down on the pumps, while F_3 was merely glowed but thoroughly degassed. During the course of the experiments, F_3 was subsequently broken down. F_2 is a tungsten ribbon $7.05\times0.0381\times0.003$ cm. Material from any filament can be vaporized onto any other filament. All the filaments were kept taut and straight by means of molybdenum springs not shown in the figure. This plate and filament assembly was inserted in one end of an appropriate lead glass tube. At the other end a Buckley ionization manometer[16] was attached. The tube was thoroughly pumped and had magnesium "get-

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[15] Becker, "The Life History of Adsorbed Atoms and Ions" Proc. Am. Electrochem. Soc. **55**, 153 (1929).

[16] Buckley, Proc. Nat. Acad. Sci. **2**, 683 (1916).

ter." After it was sealed off and cleaned up by glowing the thoriated tungsten filaments in the manometer and the broken down coated filament, the pressure was ordinarily about 1×10^{-8} mm Hg and the activity of the filaments was not affected by gas even over long periods of time.

Tube 89-B was similar to 12-J. It differed from it in three significant respects: (1) The tungsten ribbon F_W was about 10 cm long instead of 7.05 cm. This reduced the effects of end cooling. (2) The middle collector or plate was 1.27 cm high instead of 2.53 cm. This too reduced end-cooling effects and also minimized effects due to non-uniformities along the filament. (3) A movable nickel shield could be placed between the unbroken down coated filament and the other two filaments. This permitted experiments which could not be performed in 12-J.

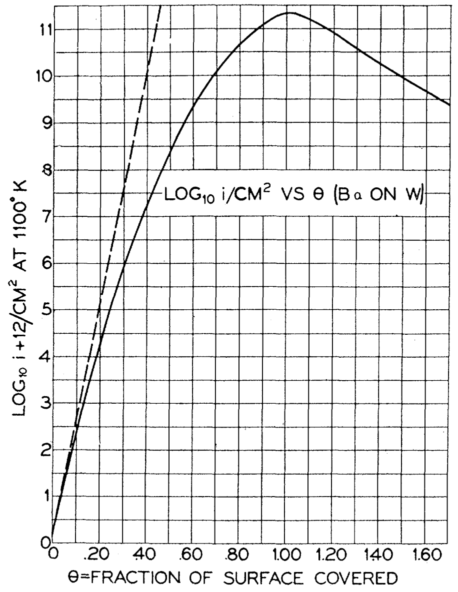

Fig. 1.

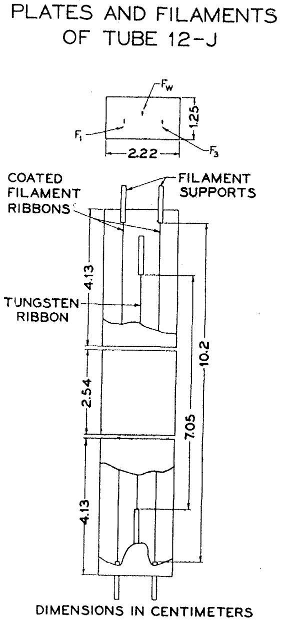

Fig. 2.

Experimental Results

The experimental results will be divided into eight groups which tend to show that: (1) Metallic barium evaporates from a well broken down coated filament; (2) Oxygen evaporates if an emission limited current is drawn and the temperature is high enough; (3) The high activity of oxide coated filament results from metallic barium on the oxide surface; (4) Barium diffuses readily to and from the surface of the oxide; (5) Oxygen affects the activity in various ways; (6) Oxygen diffuses readily to and from the surface of the oxide; (7) Most of the current through the oxide is carried by electrons but a small part is carried by ions; the ratio depends upon the temperature, the composition of the oxide, and the plate potential; (8) The complex time changes that occur can be interpreted in terms of these processes.

(1) Evaporation of metallic barium from oxide coated filaments. That metallic barium evaporates from a well broken down coated filament was shown by the following experiments. In tube 12-J, after filament F_3 had been broken down and thoroughly aged, it was glowed at 1260°K for about 10 minutes while the tungsten filament F_W, which had previously been cleaned off, was cold. F_3 and the whole tube were then allowed to cool and the activity of F_W was determined at a series of testing temperatures which were as low as possible so that no appreciable time changes took place during the test. It was found that the activity of F_W had increased appreciably. F_3 was then again glowed as previously while F_W was cold. When the tube was cool, the activity was again determined at a series of low testing temperatures. This process was repeated a number of times. Whenever necessary, the emission from F_W was extrapolated or interpolated to 1100°K.

When the log of these emission currents reduced to a cm^2 were plotted against the total time of flashing F_3 at 1260°K, a curve similar to Fig. 1 was obtained: Log i rises rapidly at first, then more and more slowly until it passes through an optimum beyond which it decreases. By appropriate experiments, it was shown that in equal intervals of time of glowing F_3, equal quantities of material were deposited on F_W so that θ, the fraction of its surface covered, is directly proportional to the time of glowing F_3 at a fixed temperature. That θ is equal to unity for the optimum activity is based on (1) analogy with caesium on tungsten for which it was proven[5] and (2) the author's theory of the emission from composite surfaces[15] from which it follows that θ should be equal to unity at the optimum activity for all electropositive materials adsorbed on strong electronegative surfaces. The exact shape of the curve in Fig. 1 was obtained by correcting the observed curve for non-uniform deposition on various portions of one side of F_W.

When F_W was subsequently glowed at 1100°K, the activity increased until it reached practically the same optimum as before; then the activity decreased and approached a steady value. When the temperature of F_W was increased again, the activity decreased, at first rapidly and then more and more slowly. This process was continued at successively higher temperatures until the activity of clean tungsten was reached at a temperature of about 1700°K.

Apparently something evaporated from F_3 and activated F_W. When F_V was subsequently heated, this something disappeared from the surface of F_W. If this whole behavior could be repeated even in some of its quantitative aspects, with a source known to contain barium, it would be fair to infer that the material that evaporated from a well broken down coated filament is barium.

This inference was established by an experiment performed by J. M. Eglin[17] of these laboratories. He built and worked with tube 5-E which was just like 12-J except that the two coated filaments were replaced by two filaments consisting of an alloy core of 95 percent platinum, 5 percent nickel and metallic barium. The barium was obtained from barium-azide and was

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[17] Eglin, Phys. Rev. **31**, 1127 (1928).

alloyed with the filaments in a separate tube by a process which is now well known.[2] If such barium alloy filaments are thoroughly aged to free them of nitrogen, and are then glowed at 1200°K, chiefly barium evaporates from them. The changes in activity of the tungsten filament obtained in this tube were just like those described in the preceding paragraphs for tube 12-J. Even more significant is the fact that the optimum activity obtained in these two tubes agreed quite closely with each other.

Figure 3 is in part intended to show how close this agreement is. It is a plot of the emission vs. the power supplied to F_W per cm^2 on a coordinate paper devised by C. J. Davisson of these laboratories. If the emission from a filament obeys Richardson's $T^{1/2}$ equation and if the watts dissipated increase with T^4, then the "power emission" line should be straight. Line No. 1 shows the observed optimum for tube 12-J. Line No. 2 is for tube 5-E. This line has been slightly corrected for the fact that the tungsten ribbons in the two tubes were not quite identical. This correction, which amounted to about a factor of 8 at the lower currents and 2 at the higher currents, was based on the power emission lines for clean tungsten and on the heating currents necessary to make the filaments barely visible in a dark room. Line No. 3 is for a similar optimum from a coated filament in tube 89-B. Note that none of the three lines is straight. This is due to the fact that at temperatures below about 1000°K, the end cooling is appreciable and becomes more marked at lower temperatures. Line 4 is line 1 corrected for end cooling by approximate methods. Since in 89-B the end-cooling correction should be less than in the other two tubes because the filament was 10 cm long instead of 7.05 cm line 3 should be everywhere higher than lines 1 and 2. The figure shows that this is so. The agreement between line 2 for barium on tungsten and lines 1 and 3 for two cases of material vaporized from well broken down coated filaments on tungsten, is almost as good as between two successive determinations of the same line. Line 5 in the lower right corner shows the emission from clean tungsten. An approximate temperature scale is added below the power scale. The close agreement of the optimum lines and the similarity of the general behavior in the three tubes make it very probable that barium evaporates from a well broken down coated filament at temperatures near 1250°K.

If in similar experiments the coated filament were not well broken down or if its temperature were too high, or if current was being drawn from it during the vaporization process, then another element presumably oxygen either free or in the form of an oxide, was vaporized over with the barium. This oxygen showed itself in the following four ways: (1) The log i vs. θ curve of Fig. 1 instead of rising rapidly and then more slowly, rose slowly and then approached the trend shown in Fig. 1. If the oxygen ratio was rather high, the activity actually decreased during the first few minutes of flashing; then it started to rise. (2) If about 0.9 layer was deposited on F_W and if F_W was then glowed at successively higher temperatures, the activity decreased to a value below that of clean tungsten. At still higher temperatures, near 1800°K the activity increased again to that of clean tungsten. This behavior is analogous to that for caesium and oxygen on tungsten.[5] (3) If more than one layer was deposited, the temperature required to pass backward through the optimum at a reasonable rate was considerably higher than if no oxygen was vaporized. The oxygen apparently holds the barium more tenaciously than does clean tungsten. This too is analogous to its behavior for caesium on oxygen on tungsten. (4) The optima were not definite but depended on the amount of oxygen coming over with the barium. Comparatively small amounts of oxygen increased the optimum line to a value of about five times that for barium on tungsten. Large amounts of oxygen lowered the optimum line more and more. This also is analogous to caesium on oxygen on tungsten, but in this case, the optimum caesium on tungsten line can be increased several hundredfold by the proper amount of oxygen.

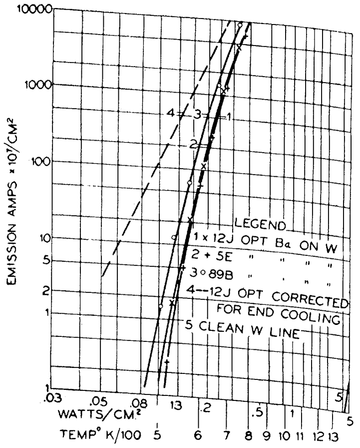

Fig. 3.

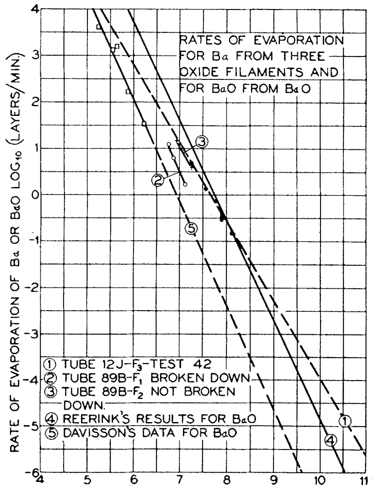

Fig. 4.

An interesting deduction from these experiments is that barium and oxygen do not permanently combine chemically on a hot tungsten surface. Another way of stating this, is that barium oxide is decomposed on a hot tungsten surface.

The peak or optimum activity phenomenon furnishes us with a convenient and powerful method for determining rates of evaporation of electropositive materials at various temperatures. All that need be done is to determine the time required for the activity of F_W to reach its optimum and to compute from the geometrical relationships the number of layers that must evaporate from the primary to deposit one layer on the tungsten. In this way the number of layers evaporating per minute at a series of temperatures was determined for several coated filaments.

In Fig. 4 the log of the evaporation rate expressed in layers per minute has been plotted as a function of $1/T$. Curves 1, 2 and 3 are for the evaporation of barium from oxide coated filaments.* Line 4 represents the data

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* θ, the fraction of the surface covered with barium may have been different from one

obtained by Reerink for barium oxide from barium oxide which was reported in an article by Zwikker.[18] The points through which line 5 has been drawn are experimental values obtained by C. J. Davisson in these laboratories several years ago. He showed also that the rate of evaporation of strontium oxide from strontium oxide was negligibly small compared to barium oxide from barium oxide. The filaments which furnished the data for line 1, 2 and 3 consisted of a mixture of barium oxide and strontium oxide. Presumably the evaporation rate of barium oxide from this mixture is somewhat less than it would have been from a pure barium oxide surface. From this and from a comparison of the slopes of lines 1 to 3, and lines 4 and 5, it follows that at low temperatures chiefly barium should evaporate while at sufficiently high temperatures chiefly oxide should evaporate.†

It should be pointed out that this method of determining evaporation rates at various temperatures might well be used for a study of the precise way in which the evaporation depends upon the temperature.

That mostly metallic barium rather than barium oxide evaporates from well broken down coated filaments follows from experiments performed by C. J. Davisson in these laboratories several years ago. It was found that the material that evaporated produced rather large resistance leaks across glass surfaces between metallic terminals. When air was let into such tubes, the resistance increased greatly and rapidly. Commercial hydrogen, presumably slightly impure, caused no rapid changes in resistance. Metallic barium would be expected to produce these results while barium oxide would not.

These experiments, it seems to us, prove conclusively that metallic barium evaporates from a well broken down oxide coated filament. If the temperature is not too high and if no electrons are drawn from the filament, it appears that practically nothing else evaporates. At sufficiently high temperatures barium oxide must also evaporate.

(2) Evaporation of oxygen. When current is drawn from a coated filament at a sufficiently high temperature and if this current is not limited by space charge, oxygen evaporates. Some of this oxygen is deposited on the tungsten ribbon in Fig. 2 and decreases its activity. Thus, when filament F_3 in tube 12-J was at a temperature of about 800°K and the plates were at a positive potential of about 100 volts, it was found that the activity of the tungsten ribbon decreased progressively. In one particular case, the current to the center plate was about 1.0 milliampere and the activity of the tungsten ribbon was decreased by a factor of two for every 2 hours. By drawing large currents we have been able to reduce the activity of the tungsten filament by a factor of 200.* If the tungsten ribbon was subsequently raised to tempera-

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filament to the next but for a given filament it was probably quite constant since the activity did not change appreciably with changes in glowing temperature.

[18] Zwikker, Physica **8**, 241, (1928).

† At about 1250°K the evaporation rate of barium from metallic barium is about 10^8 times as great as the rate of evaporation of barium from a well broken down coated filament.

* From the fact that the activity of the tungsten ribbon can be reduced by more than a factor of two, we may conclude that the oxygen which strikes one side of the ribbon must

tures higher than about 1600°K, the activity increased for a time and then became almost constant. If the temperature was raised again, the activity increased rapidly at first and then more and more slowly.** At 1800°K, the activity reached that of clean tungsten in something like ten minutes.

Practically all of this oxygen must leave the coated filament in an uncharged condition, for the rate at which it collects on the tungsten ribbon is not affected by the potential of the tungsten ribbon. If an appreciable amount of the oxygen were negatively charged and if the tungsten ribbon were made negative with respect to the coated filament, the rate of deactivation of the tungsten ribbon should be appreciably decreased. We have made several experiments in several tubes to test this point and have never found any evidence that the oxygen was negatively charged. This is rather surprising in view of Barton's result[19] which is frequently quoted in the literature. It may be that the condition of his filament was considerably different from that of ours and from that in ordinary tubes.

By determining the rate of deactivation of the tungsten ribbon as a result of various treatments imposed upon the coated filaments, it is a rather simple matter to determine the factors upon which the rate of evaporation of oxygen depends. Such experiments have shown that the rate of oxygen evaporation increases with (1) the temperature of the filament, (2) the amount of current drawn from it, (3) the plate potential and (4) the composition or state of the oxide. Thus far, the exact manner in which it depends on these factors has not been determined accurately. The first two factors were to be expected. That the oxygen evaporation increases rapidly with the positive plate potential is somewhat surprising since one might expect the potential difference across the oxide at a given temperature to depend only on the current through it. Experiment, however, shows very definitely that if the emission is limited by space charge, no oxygen or very little oxygen is liberated compared to the amount liberated when the plate voltage is increased such that the current is limited by emission. When the plate is at a negative potential, no oxygen evaporates. It should be pointed out that the temperatures at which it is possible to obtain oxygen at an appreciable rate are considerably lower than those required to obtain barium at an appreciable rate. It is therefore possible to obtain oxygen without barium by one procedure, and barium without oxygen by another.

An important observation was this: it was comparatively easy to obtain oxygen from filament F_3, the unbroken down coated filament in tube 12-J, soon after the tube was sealed off the pumps. However, after a considerable quantity of oxygen had been removed and the filament had become more active, it required large currents, 10 to 20 mils, and high plate potentials, 150 to 200 volts, to obtain appreciable quantities of oxygen. We take this

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migrate and reach the other side of the ribbon at the testing temperatures of about 1400°K. Subsidiary experiments especially with the shielded tube 89-B showed that no oxygen could reach the back side of the tungsten ribbon by being reflected from the walls of the tube.

** The reason for this behavior is that the rate of evaporation at a given temperature decreases rapidly as θ decreases.

[19] Barton, Phys. Rev. **26,** 360 (1925).

to mean that originally an appreciable part of the current through the oxide was carried electrolytically by oxygen and barium ions; after the filament was broken down and barium was dispersed through the oxide, a much smaller part of the current was carried by ions.

From the experiments described in this section, we conclude that when current is drawn from a coated filament at a sufficiently high temperature and this current is not limited by space charge, oxygen evaporates. Most of this oxygen must be uncharged. The rate at which it appears increases rapidly with the plate potential, and it decreases as more barium is dispersed through the oxide.

(3 Activation due to barium on barium oxide. There are two ways by which barium can be caused to appear at the surface of the oxide: one is by sending electrons into the oxide from an outside source and thereby electrolizing the oxide; the second is by vaporizing barium from another filament which, under proper conditions, may be another oxide coated filament. The barium which is thus brought to the surface of the oxide should change the activity of the filament. If barium on barium oxide is analogous to barium on tungsten the log of the activity should increase rapidly at first, then more and more slowly until it passes through an optimum beyond which it should decrease. When the oxide coated filament is subsequently glowed and the barium is thereby caused to diffuse or vaporize from the surface, the activity should again increase to an optimum and then decrease to its normal value. The following experiments and figures show that this is exactly what happens.

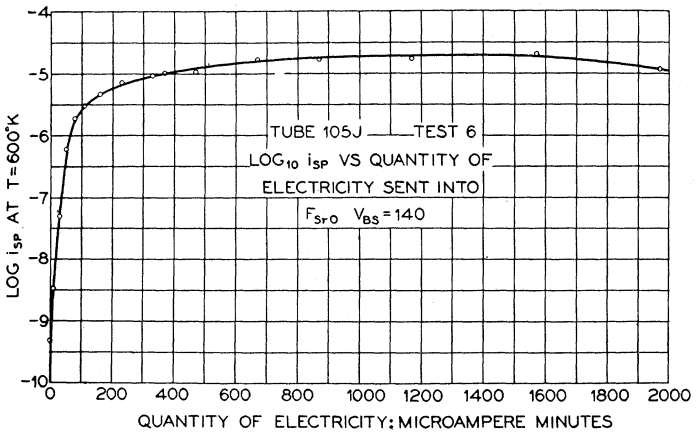

Fig. 5.

Figure 5 shows a logarithmic plot of the activity of a strontium oxide uncombined filament as a function of the amount of electricity, expressed in microampere minutes, sent into it from an outside source through a P. D. of 140 volts. The activity is here defined as the emission current from the entire 10 cm length of the filament at approximately 600°K and 70 volts plate potential. For some points this activity was determined by extrapolation from higher or lower temperatures. Note that the activity increased to an optimum value which was about 30,000 times its initial value after about 1200 microampere minutes had been sent into the filament. Subsidiary tests showed that all parts of the filament did not reach their optimum at the same time. This causes the peak to be considerably flatter and somewhat lower than it would otherwise be. Such non-uniformities are to be expected and are extremely difficult to avoid. If they had been avoided, we estimate that the optimum would have come at 300 mic-minutes. Subsidiary tests also showed that the initial test point in Fig. 5 did not correspond to clean strontium oxide, for subsequent more severe glowing reduced the activity below this value. If the current through the oxide were entirely electrolytic and if the microscopic surface area were the same as the measured macroscopic area, about 2.0 microampere minutes per cm^2 should suffice to cover the surface with a monatomic layer of metallic strontium. From these facts we may conclude that very roughly 1/200 of the current through this particular oxide was carried by strontium ions.

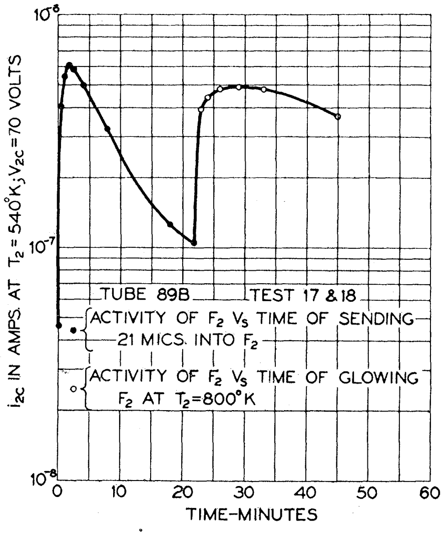

Fig. 6.

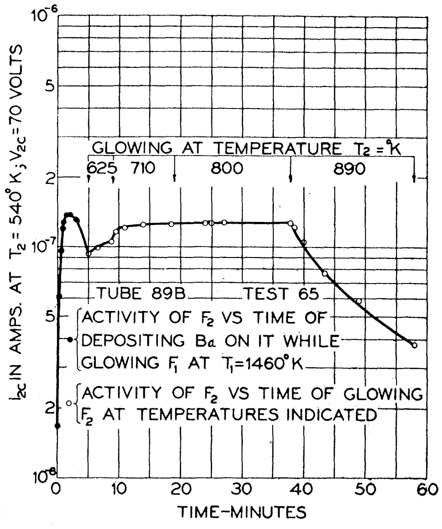

Fig. 7.

The first part of Fig. 6 shows a similar curve for test 17, tube 89-B, filament F_2. In this case 21 microamperes were sent into the coated filament for a total of 22 minutes. At the end of this time F_2 was glowed at 800°K for 23 minutes. The activity was tested under standard conditions at the times for which points are plotted. The activity passed through an optimum which is about 25 percent lower than the optimum for the preceding curve. This small discrepancy in the optima is no greater than is usual in this type of curve and is possibly due to slight differences in the degree of uniformity of covering.

If we compare Figs. 5 and 6 we note that the peak is much sharper in 6 than in 5. This is undoubtedly due to the fact that in Fig. 6 the degree of non-uniformity at the peak is much less than it is in Fig. 5 since the activity in Fig. 6 refers to 1.27 cm of the center portion of the filament while that in Fig. 5 refers to the entire 10 cm length.

A still more striking difference between these two figures is that in Fig. 6 the optimum activity is only about 13 times the initial activity while in Fig. 5 it is about 30,000 times the initial activity. This is undoubtedly due to the fact that in Fig. 6 the filament surface was nearly completely covered with barium at the initial activity.

The proof of this statement is based on test 61A, tube 89-B. In this test the broken down coated filament F_1 was flashed at 1450°K in order to vaporize barium onto F_2 and also onto F_W. (See Fig. 2 for the relative positions of the oxide coated and tungsten filaments.) The activity of F_2 changed in the manner practically identical with that given in the first part of Fig. 7 for test 65 except that the curve was extended for 20 minutes instead of 5; from 5 to 20 minutes it decreased at a slower and slower rate. During the same time the activity of F_W followed a course given by Fig. 1, the peak occurring after 14 minutes of flashing F_1. Note that F_2 reached its optimum activity before two minutes of flashing while F_W reached its optimum after 14 minutes. Since F_2 was about twice as far from F_1 as was F_W from F_1, the amount of material reaching F_2 in a given time is about 1/2 as great as that reaching F_W. Consequently it required only 1/14 or about 7 percent as much material to bring F_2 to its optimum as it did to cover F_W with a monatomic layer. On the hypothesis that the optimum activity occurs at a monatomic layer, we may conclude that F_2 was 93 percent covered at the initial value in Fig. 7. This initial value could be repeatedly obtained after glowing at about 1300°K for several minutes, and was roughly the same as in Fig. 6.

Fig. 7 shows the change in activity of F_2 while F_1 was glowed at 1460°K for 5 minutes. Note that the activity passes through an optimum after barium is deposited on F_2. Subsequent glowing of F_2, at the temperatures and times indicated in Fig. 7, caused the activity to pass through practically the same optimum as before.

It is very instructive to compare Figs. 6 and 7. In one case barium was brought to the surface by electrolysis while in the second case it was deposited by vaporization. In both cases the activity of F_2 passed through an optimum. In both cases subsequent glowing caused the activity to go backward through an optimum practically equal to that of the optimum which preceded it. The slight differences between the two cases are easily accounted for by the treatment given the filament between tests 17 and 65. Unfortunately we do not yet have two such curves for the filament in identical conditions and especially in an initially rather inactive state.

That the amount of barium brought to the surface by electrolysis is directly proportional to the quantity of electricity sent into the oxide coated filament may be inferred from Fig. 8. This is a plot of the logarithm of the emission from the central inch of filament F_3 at a temperature of 475°K and a plate voltage of 31.5 volts vs. the mic-minutes of current sent into F_3 while F_3 was at 475°K. Each set of points shown in this figure represents a complete curve by itself. For one set of points, the current sent into the filament was 6.0 microamperes; for others, 15, 60, and 380 microamperes respectively. From the fact that the different sets of points all fall on the same curve, we may conclude that the number of ions brought to the surface depends only on the product of the current and the time and not upon either variable alone. This is readily understandable if the amount of barium brought to the surface is directly proportional to the quantity of electricity sent into the filament.

In Fig. 8 the initial activity is very close to the optimum activity. While we have no proof in this particular instance that this means that the surface is practically completely covered, we have no hesitation in inferring this from analogy with the data discussed above for tube 89-B. Similar data in tube 12-J could not be obtained since the filament F_1 was burned out rather early in the history of the tube. Before the curve shown in Fig. 8 was taken, filament F_3 had been well activated by breaking it down. Its activity could not be decreased appreciably by glowing it even at fairly high temperatures such as 1300°K for a time sufficient to vaporize hundreds of layers of barium from it. Possibly by glowing it at temperatures near the melting point of the core, we might have decreased the activity slightly.

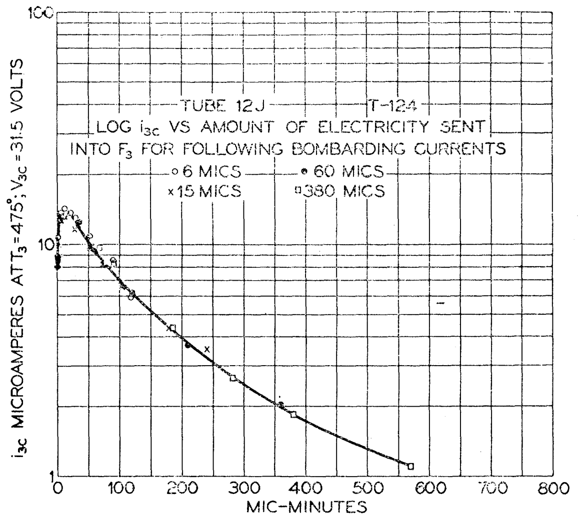

Fig. 8.

While we have no curve showing the rise in activity of F_3 while barium was being vaporized onto it from F_1, we do have a curve which shows what happened to the activity of F_3 after about three layers of barium had been deposited on it. This is shown in Fig. 9 in the form of power emission curves. The line or lines on the extreme right show the initial activity in test 1 soon after the tube was pumped. After about three layers of barium had been vaporized onto F_3, the emission was that given by points 1 and 2 in the lower left-hand corner of the figure. Even at as low a temperature as 500°K the activity increased due to barium disappearing from the surface. At any temperature such time changes were usually rapid at first and then slowed down until they were fairly steady.* The temperature was then changed to a higher value at which the activity increased again. This process continued up to points 7 and 8. For still higher temperatures the activity decreased at each temperature. After point 12 the temperature was decreased. At the lower temperature the activity was now quite steady. In this condition the activity was still appreciably higher than it was in the initial state, presumably because some barium was still left on the surface even after glowing at approximately 1000°K. Note that the maximum line is about 100,000 times as active as the initial line. By subsequent treatment of the filament, the activity was raised almost to that of the optimum line given in the upper left corner. This line is about 10^7 times as active as the initial line.

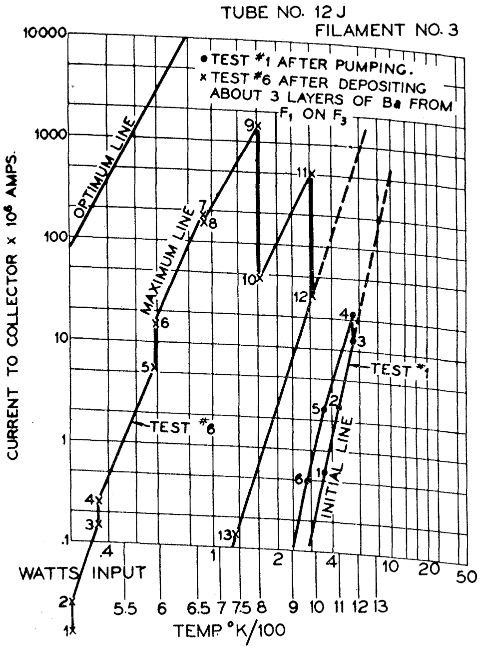

Fig. 9.

The evidence presented in connection with Figs. 5, 6, 7, 8, and 9, proves conclusively that the activity of an oxide coated filament can be greatly modified by depositing barium on its surface. We could give many more curves similar to the ones which have been given, but feel that this is unnecessary.

The amount of barium on the surface of the oxide is not the only factor which determines the activity, for otherwise the activity of all oxide coated filaments should be the same for an optimum amount of barium on the surface. Experiment shows that this is not so. The optimum line for filament

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* The reason for this behavior is that the rate of evaporation at a given temperature decreases rapidly as θ decreases.

F_3 in tube 12-J is shown in Fig. 9. The optimum line for F_2 in tube 89-B was approximately parallel to this line but was a factor of 25 below it. The optimum line for filament F_1 tube 89-B, was again approximately parallel to the optimum line for F_3 tube 12-J, but was a factor of 500 below it. That the optimum lines for the same filament at various stages of its breakdown process may differ is suggested by the position of the "maximum line" and "optimum line" in Fig. 9. There is some question as to the part that oxygen played in the determination of the "maximum line," but for this line as well as for the "optimum line," the surface was quite likely covered with an optimum amount of barium.

(4) Diffusion of barium in the oxide. That the barium which is produced by electrolysis diffuses into and through the oxide can be deduced from a number of experimental facts. One of these is the activation resulting from the breakdown process. The barium is deposited on the oxide-core interface and must diffuse through the oxide to the surface before it can increase the activity.

Another argument for diffusion is this; hundreds of layers of barium can be vaporized from a well broken down filament without appreciably altering its appearance or its activity. This barium could not possibly have been on the surface of the oxide at one and the same time, for otherwise, (1) the surface would have had a metallic appearance, (2) the activity could not have been affected by adding more barium, and (3) the rate of vaporization would have been much higher than was found to be the case. Hence the barium must have diffused through the oxide to the surface.

A semi-quantitative proof of diffusion is based on the life of these filaments. It is a well-established fact that these filaments retain an appreciable percentage of the original oxide even after furnishing a current of 20 milliamperes from a cm^2 for at least two years or approximately 15,000 hours. We shall show below that more than one part in one thousand of the current through the oxide is carried by ions. Hence at 15,000 hours, 300 milliampere hours or 18,000 milliampere minutes of ion current must have reached the surface. If each ion carries a charge equal to that on the electron and if a single layer of barium corresponds to about 7×10^{14} atoms per cm^2, it requires about two microampere minutes of ion current per cm^2 to produce one layer. Hence the number of layers of barium that should be deposited at the current and time specified above is more than 9,000,000. Actually there are only about 20,000 layers of oxide on a filament and only a portion of these disappear during the treatment. Hence it follows that by far the largest part, about 0.998, of the barium which is produced by electrolysis must diffuse into the oxide, and must recombine with oxygen to form barium oxide.

The rate at which the barium diffuses from the surface into the oxide may be determined from curves such as that shown in the second part of Fig. 6. In this case the surface concentration of barium was greater than that corresponding to equilibrium conditions and hence the barium disappeared from the surface rapidly at first and then more slowly. This barium either evaporated or diffused into the oxide. That only a small part evaporated appears from the following calculation. In Fig. 6 we estimate that at 800°K about 0.05 layers left the surface between times 30 and 45 minutes. This corresponds to a rate of one layer in 300 minutes or about 3×10^{-3} layers per minute for an average θ of about 0.98. From curve 3 in Fig. 4 for which θ was about 0.90 we can obtain that at 800°K, the rate of evaporation was about 3×10^{-7} layers per minute or only 1/10,000 of the rate of disappearance. It seems improbable that the evaporation rate increases as much as one thousand-fold when θ changes from 0.90 to 0.98. Hence most of the barium must have left the surface by diffusion and the diffusion rate must be approximately the same as the total rate of disappearance.

Whenever the barium surface concentration exceeds the equilibrium concentration, the rate at which the surface concentration approaches the equilibrium concentration is rapid at first and then decreases more and more. This is readily deduced from the shapes of the glowing curves like those in Figs. 6 and 7. One would hardly expect that the diffusion inward should cease when the equilibrium concentration is reached. It appears very likely that there is a constant interchange of atoms between the surface and the interior of the oxide. We should expect that the rate of diffusion to the surface should be directly proportional to the volume concentration of barium in the oxide while the rate of diffusion from the surface should increase exponentially with the absolute value of the surface concentration. The latter expectation is based on the picture that it takes a definite amount of work to take an atom from the surface into the interior and that this amount of work decreases as the surface concentration increases; in other words, that the diffusion inward process is analogous to the evaporation process.* When a steady state is reached at any glowing temperature just as many atoms come to the surface as leave the surface. From this picture we should expect that the surface concentration should not differ greatly when the volume concentration is changed by even as great a factor as 10. This may explain why the activity is not very greatly dependent on the amount of barium stored in the core and oxide coating.

(5) The effect of oxygen on the activity. It is a well-known fact that when current is drawn from a coated filament the activity of this filament changes rapidly at first and then more and more slowly. The magnitude and even the direction of the change in activity depend greatly upon the composition of the oxide, the plate potential, the degree of breakdown and the temperature of the filament.

For a well broken down filament we have invariably found that the activity decreases rapidly and then more and more slowly. This is illustrated in the first part of Fig. 10. Curve 1 shows how the emission current in milliamperes decreased at a temperature of 715°K and 60 volts plate potential. At intervals the activity was tested at a lower temperature, 475°K. This activity is plotted in microamperes as curve 2.

It was shown above that if the temperature and the plate potential are high, oxygen is formed by electrolysis and evaporates. Presumably, there-

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* See reference 15. The reason for this behavior is, that the rate of evaporation at a given temperature decreases rapidly as θ decreases.

fore, the decay in activity is caused by oxygen which has come to the surface and some of which stays there because the temperature does not remove it rapidly. Because of its electron affinity some of the oxygen should be negatively charged and if the oxygen stays on top of the surface layer of barium it should produce electrical fields which hinder the escape of electrons. Consequently the activity should decrease. If more and more oxygen is brought to the surface the rate at which it disappears from the surface either by evaporation or by diffusion should increase rapidly until the rate of disappearance is equal to the rate of production. We thus have a satisfactory picture of the cause of the decay in activity when current is drawn.

This view is supported by experiments in which oxygen was vaporized onto the broken down filament from another oxide filament. The activity of the broken down filament was reduced by more than a factor of ten. The slope of the log i vs. θ curve was practically constant while the activity decreased by a factor of five; then the slope gradually became less.

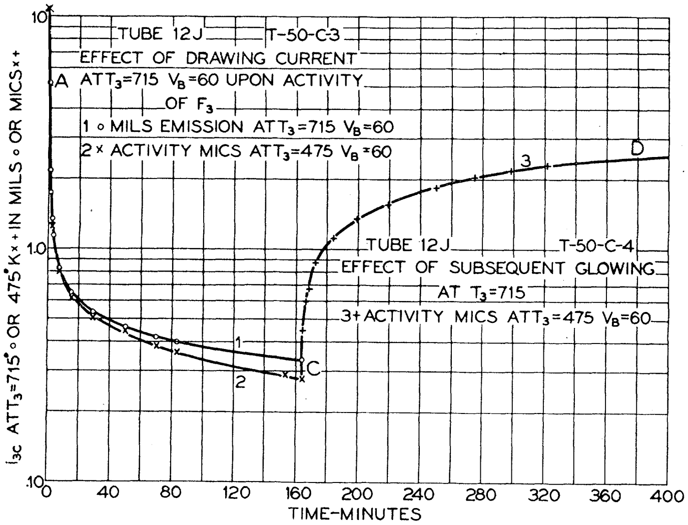

Fig. 10.

Of course, one could postulate that the oxygen which comes to the surface combines with the barium and decreases the activity by decreasing the surface barium concentration. This, however, is unlikely since it was shown above that barium and oxygen do not permanently combine chemically when they are present on a hot tungsten surface. Even more convincing is the experimental fact (test 34, tube 89-B) that when the barium concentration was more than the optimum and oxygen was then brought to the surface, the activity decreased rather than increased. If the oxygen combines with the barium, the barium concentration should decrease and thus come nearer to the optimum concentration which should result in an increase in the activity.

If the filament is merely glowed at the same temperature at which current has been previously drawn the activity increases rapidly at first and then more and more slowly. This is illustrated by curve 3 in Fig. 10. In general the activity either never or only extremely slowly reaches the initial activity. If, however, the filament is glowed at a high temperature such as 1200°K, the initial activity can be readily restored.

The explanation for this activation on glowing is fairly apparent. Some of the oxygen which was deposited on the surface by electrolysis is caused to leave the surface by thermal agitation. As the oxygen surface concentration gets nearer and nearer to its equilibrium value, the rate of disappearance of the oxygen decreases more and more.

Thus far we have described the effects of oxygen on the activity in a well broken down filament. We shall now proceed with the effects of oxygen in filaments which have not been broken down. The best data on this subject were obtained with an uncombined strontium oxide filament. The results were confirmed with an uncombined barium oxide filament and to some extent in a barium oxide plus strontium oxide combined filament. They are thus quite general and well established even though similar results have never been reported in the literature.

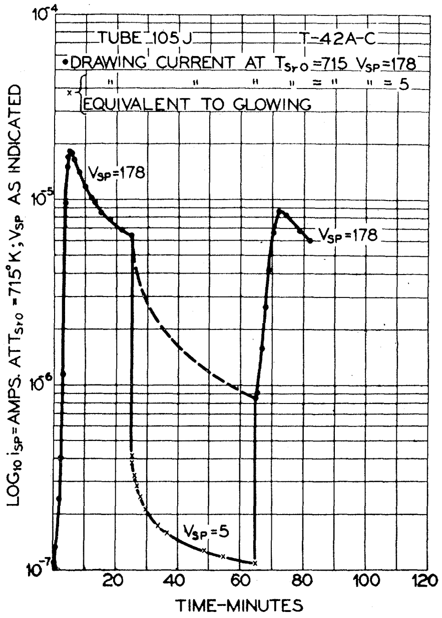

Fig. 11.

When current was drawn from the unbroken down strontium oxide filament in tube 105-J at a temperature less than 950°K and a plate potential of 178 volts, the log of the emission increased slowly, then more rapidly, then more slowly again until it reached a peak or maximum value beyond which it decreased and asymptotically approached a steady value. A typical curve is shown in the first part of Fig. 11. The rate of activation and the height of the peak increased considerably with the plate potential. For sufficiently small plate potentials such as 30 volts the activity never passed through a peak value but merely increased to its steady value.

When the filament was glowed at the same temperature at which current had been drawn, the activity decreased rapidly at first, then more and more slowly. This activity was determined under testing conditions which did not alter the activity: either both the temperature and the plate potential were decreased, or else the plate potential alone was decreased to a low value. The solid line in the second part of Fig. 11 shows the decrease in the activity when the plate potential was reduced to 5.0 volts. The dashed line above this solid line shows the instantaneous emission that would have occurred if the plate potential had been changed back to 178 volts at any particular instant. This was actually done at time 65 minutes with the result shown in the third part of the figure. A peak was again obtained, but this peak was lower and occurred later than the first peak. In order to duplicate the first curve it was found necessary to glow the filament at a much higher temperature such as 1200°K for 5 or 10 minutes.

If the data of the first curve in Fig. 11 are used to plot a curve of the log of the activity vs. mic-minutes of current drawn from the filament, a straight line is obtained for the initial portion of the curve. The slope of this line is a measure of the rate at which some activating material is coming to the surface. A series of experiments has shown that the slope of this line (1) increased rapidly with the plate potential, (2), decreased as the temperature increased, (3) increased when the surface was slightly covered with an active material vaporized from the plates, (4) decreased if the filament was not thoroughly glowed after the preceding test, (5) decreased markedly as the degree of breakdown increased. The height of the peak emission divided by the initial emission varied in this same manner with these five factors. The mic-minutes required to reach the peak (1) decreased with the plate potential (2) decreased as T increased, (3) and (4) changed slightly with the third and fourth factor given above, (5) decreased from about 20 to about 2 mic-minutes per cm^2 when the filament was broken down. In the case of a barium oxide uncombined filament in tube 123-J the peak came at about 60 mic-minutes per cm^2.

At first sight it might appear that this peak was due to barium as in the case of Figs. 5, 6 and 7. The following reasons show that this cannot be so: (1) the barium is deposited on the core and the temperature is so low that it seems highly improbable for the barium to diffuse rapidly enough to the surface of the oxide to account for the rapid increase in activity; (2) the glowing curve in Fig. 11 decreases rather than increases as it did in Figs. 6 and 7; (3) the activity at the peak is very variable and depends on the conditions prevailing during the treatment while in the barium case the optimum activity does not depend on these same conditions; (4) the optimum activity due to barium is about 50,000 times the initial activity while for this peak phenomenon the peak activity is less than 1000 times the initial activity.

The hypothesis which we tentatively propose for this peak on drawing current is an extension of what is already known. Due to electrolysis, oxygen is brought to the surface. As will be shown below the factors that determine the amount of electrolysis are of the same sort as those that determine this peak phenomenon namely, plate potential, temperature and composition of the oxide. Hence it is natural to ascribe this peak phenomenon to oxygen. From analogy with caesium on tungsten it is to be expected that a little oxygen increases the activity while more oxygen decreases it. Whether the activity is increased or decreased depends upon just where the oxygen is located with reference to the surface barium atoms. If the oxygen is beneath the barium layer, the activity is raised because the negative oxygen induces more positive barium ions and the moment of the additional barium ions and their images more than counterbalances the moment of the oxygen ions and images. If on the other hand, the oxygen is on top of the surface layer of barium, the activity is decreased because now the moment due to the oxygen is greater than the moment due to the barium.

By combining the hypothesis with the experimental facts we may draw the following conclusions: oxygen is deposited by electrolysis just beneath the partial surface layer of metallic barium or strontium. If the temperature is high enough some or all of this oxygen rather rapidly arrives at the top of the barium layer where it forms an outer oxygen layer which is a more stable layer than the inner oxygen layer. If the temperature is low enough the first oxygen that is deposited stays in the inner layer. As the oxygen concentration increases, the field tending to pull electrons and negative oxygen ions toward the plane of the barium ions increases and some of the oxygen reaches the top of the barium layer. At the peak the factors tending to increase the activity are balanced by those tending to decrease it. Beyond the peak the net result of electrolysis is the increase in concentration of the outer layer of oxygen. We believe that some of the oxygen also diffuses inward into the oxide. If the filament is glowed either before or after the peak, oxygen leaves the inner layer; it reaches the outer layer or diffuses into the oxide.

To be consistent we need to apply this hypothesis to the case of well broken down filaments in which emission is accompanied by a decrease in activity. For well broken down filaments the field which tends to pull electrons and also negative ions into and beyond the plane of the positive Ba ions is very great so that even at very low temperatures the oxygen is rapidly pulled into the outer layer. It may also be that in well broken down filaments the inner oxygen layer is already near its maximum concentration, and any additional oxygen is forced to go to the outer layer. This latter view would fit in well with the observed fact that the maximum activity which can be obtained depends on one or more factors besides the optimum amount of barium. The study of the effect of oxygen on the activity is still far from complete.

(6) Diffusion of oxygen. That oxygen diffuses from the surface into the oxide follows from the same sort of evidence as that presented above for the diffusion of barium. The argument which was presented there and which was based on the life of the filament can be applied word for word for oxygen.

Another line of evidence for the diffusion of oxygen is this: if current is drawn from a broken down coated filament even at as low a temperature as 550°K the activity decreases. After the decrease amounts to a factor of about three, the filament can be glowed at this same temperature. It is then found that the activity increases due to the glowing. This increase in activity is presumably due to the disappearance of oxygen from the surface. We should hardly expect oxygen to evaporate under these conditions: at any rate, we have never been able to detect it. Consequently we must conclude that the oxygen diffuses into the interior of the oxide.

As more and more oxygen diffuses into the interior the concentration of oxygen in the oxide increases. Some of this oxygen presumably recombines with metallic barium; some of the oxygen must diffuse back to the surface at a rate which is presumably proportional to the concentration of oxygen in the oxide. If current is drawn from the filament for a long time at a constant temperature and plate potential, the net diffusion inward decreases and may eventually approach zero especially if the temperature is high enough so that oxygen evaporates.

(7) Factors which determine the amount of electrolysis. Only a relatively small part of the current through the oxide can be carried by positive barium ions and negative oxygen ions. The ratio of ion current to total current for barium is not necessarily the same as for oxygen. For barium this ratio depends upon the temperature and the composition of the oxide; it is independent of the speed with which electrons from the outside strike the filament. For oxygen this ratio depends upon the composition of the oxide and the field strength at the surface of the filament when current is drawn from it; presumably it also varies with the temperature.

The ratio barium ion current to total current can be determined from the data for curves like those in Figs. 5, 6 and 8. The calculations based on Fig. 5 are given above: it was found that roughly one part in 200 of the current was carried by strontium ions. A similar computation for Fig. 6 leads to the conclusion that in this case 1/240 of the current is carried by barium ions. For this calculation we have used the following data: at the initial activity the fraction of the surface covered with barium was 0.90 while at the optimum it was 1.00; this 0.1 layer was deposited in 36 mic-minutes or 48 mic-minutes per cm^2; 2 mic-minutes per cm^2 of ion current were taken to correspond to one layer. A similar computation for Fig. 8 gave the result that about 1/300 of the current was carried by barium ions.

A series of tests showed that when the temperature of the coated filament was purposely raised above that prevailing in the tube while electrons were sent into it, a curve was obtained which was similar to that in Fig. 8 except that the mic-minute axis was increased by a constant factor. From this we conclude that the ratio of barium ion current to total current decreases by about a factor of 2.0 when the temperature is increased from about 300°K to about 600°K.

In another series of tests it was shown that the curve similar to that in Fig. 8 did not depend upon the potential of the oxide coated filament with respect to the source of the electrons. To obtain this result, it was however, necessary that the distribution of the current from one filament to the other was not altered when the potential between the filaments was changed.

Hence, the amount of electrolysis is not dependent upon the speed with which the electrons strike the oxide.

Our knowledge of the factors that determine the ratio of oxygen ion current to total current is based partly on the factors that determine the rate of evaporation of oxygen which were discussed in a previous section. It was there shown that the evaporation rate depended greatly on the composition or state of the oxide and also on the plate potential. Presumably the rate of oxygen production varies in the same manner as the rate of evaporation.

The rate of oxygen production was also studied by determining the decrease in log i as a function of the mic-minutes drawn from the filament. The initial slope of a plot of these variables is a measure of the oxygen ion current to the total current. From a large number of tests it follows that this ratio decreases with the degree of breakdown of the filament. Presumably this means that as more and more metallic barium is dispersed through the oxide a larger and larger proportion of the current is carried by electrons.

Another series of tests on about 10 different filaments has shown that the amount of oxygen produced per milliampere minute increases rapidly with the positive plate potential and that if the current is limited by space charge comparatively little oxygen is produced. This conclusion is again based on the initial slopes of log i vs. milliampere minute curves.

It has been tacitly assumed that the rate of oxygen production varies directly with the electron current. This tacit assumption is difficult to prove since every factor which changes the emission current seems at the same time to change the rate of oxygen production. Since, however, it is shown above that the rate of barium production is directly proportional to the electron current, we can quite safely assume that the rate of oxygen production is also directly proportional to the current.

The fact that the oxygen yield depends so markedly on the plate potential presumably means that part of the potential difference between the filament and plate is used up in the oxide but that the P.D. across the oxide is not directly proportional to the electron current through the oxide. In other words, the conductivity of the oxide does not obey Ohm's law. From the fact that little or no electrolysis takes place when the current is limited by space charge, we are inclined to believe that there is little or no potential difference across the oxide in this case. The electrons get through the oxide not because of a field in the oxide but because of a diffusion pressure similar to that which has been shown to exist in an arc.

We have no evidence at present that the oxygen yield varies with the temperature but from analogy with the barium yield, it seems probable that the oxygen yield per milliampere minute decreases somewhat as the temperature increases.

(8) Time changes in coated filaments. A rather complete study has been made of the changes in emission that occur in time as a function of the temperature, the plate potential, the immediate previous treatment and the remote but violent previous treatment. This has been done for various types of filament. We shall first describe the time changes that occur in a barium

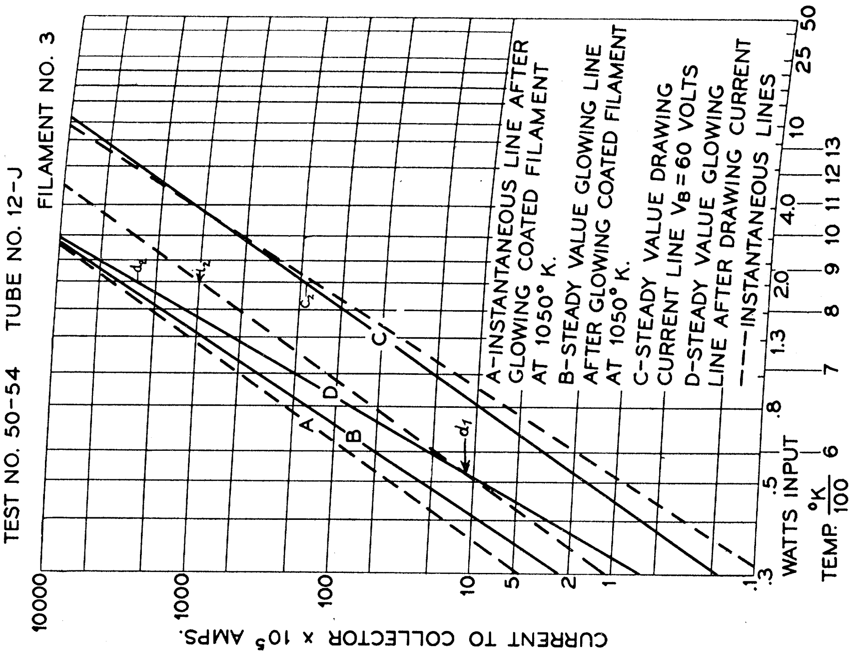
TEST NO. 50-54 TUBE NO. 12-J FILAMENT NO. 3
CURRENT TO COLLECTOR × 10⁵ AMPS.
10000
1000
100
10
5
2
1
.1
WATTS INPUT
TEMP. °K/100
.3
.5
.8
1.3
2.0
4.0
10
25
50
6
7
8
9
10
11
12
13
A
B
C
D
C_2
d_1
d_2
i_2
A-INSTANTANEOUS LINE AFTER GLOWING COATED FILAMENT AT 1050° K.
B-STEADY VALUE GLOWING LINE AFTER GLOWING COATED FILAMENT AT 1050° K.
C-STEADY VALUE DRAWING CURRENT LINE V_B=60 VOLTS
D-STEADY VALUE GLOWING LINE AFTER DRAWING CURRENT
---INSTANTANEOUS LINES

Fig. 12.

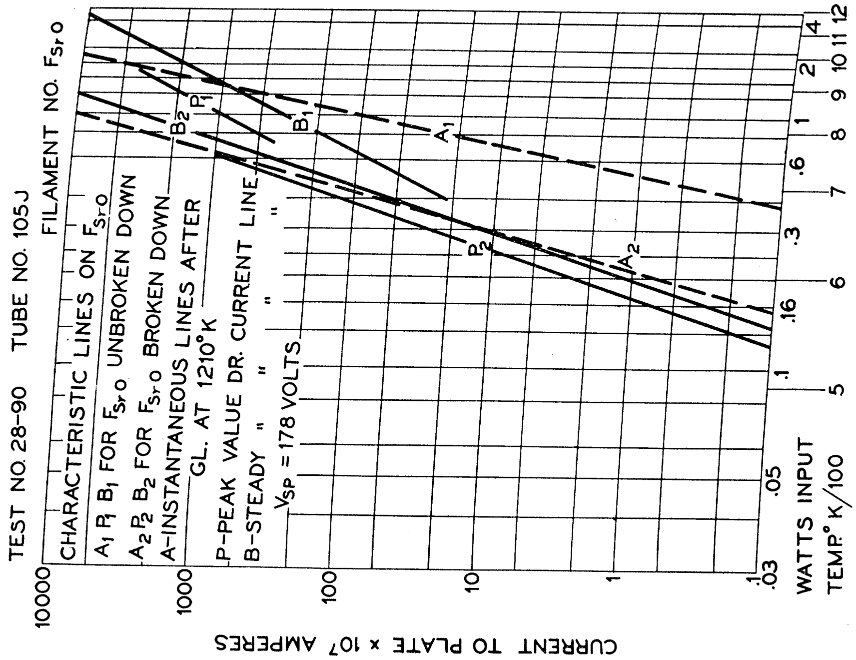
TEST NO. 28-90 TUBE NO. 105J FILAMENT NO. F_{SrO}
CURRENT TO PLATE × 10⁷ AMPERES
10000
1000
100
10
1
.1
WATTS INPUT
TEMP.° K/100
.03
.05
.1
.16
.3
.6
1
2
4
5
6
7
8
9
10
11
12
A_1
P_1
B_1
A_2
P_2
B_2
CHARACTERISTIC LINES ON F_{SrO}
A_1 P_1 B_1 FOR F_{SrO} UNBROKEN DOWN
A_2 P_2 B_2 FOR F_{SrO} BROKEN DOWN
A-INSTANTANEOUS LINES AFTER GL. AT 1210° K
P-PEAK VALUE DR. CURRENT LINE
B-STEADY " " "
V_{SP} =178 VOLTS

Fig. 13.

oxide+strontium oxide combined broken down filament. Then we shall discuss the changes in an uncombined filament, first, before breakdown and later after some breakdown has occurred.

These time changes can best be described in terms of power emission curves. It was first found that the effect of any immediate previous history of the filament could be wiped out by a one to ten minute glowing at about 1050°K. The activity at a low testing temperature could repeatedly be restored to a definite value by this treatment. In the case of filament F_3 tube 12-J, this activity is represented by the uppermost dashed line *A* in Fig. 12. Since the emission decreased when current was drawn, it was in some cases necessary to extrapolate the current to zero time. At low temperatures the time changes are so slow that this need not be done. A typical decay curve has been shown in curve 1 of Fig. 10 for a temperature of 715°K. If current is drawn for a sufficiently long time, these decay curves become practically flat. The emission for this steady value on drawing current is represented by a point on line *C* Fig. 12 at the treating temperature. By glowing at 1050°K and drawing current at other deactivating temperatures until the emission became practically steady, other points on the *C* or steady value drawing current line were obtained.

If the filament is glowed at the treating temperature after a point on the *C* line has been obtained, the emission increases rapidly at first then more and more slowly until it becomes practically flat. This is illustrated by curve 3 in Fig.10. The emission for this flat porton of the curve is then plotted against the treating temperature, and a series of such points at various temperatures constitute the *D* line in Fig. 12.

The rate at which these time changes take place increases rapidly as the temperature is increased. Thus at a temperature of 600°K it might take something like 10 hours to go from a point on the *A* line to a corresponding point on the *C* line, while at 900°K it would take only several minutes for the same transition.

If at any stage in a deactivation curve (*A-C*) or a subsequent activation curve (*C-D*) the temperature is suddenly changed to a higher or to a lower value and if the instantaneous emission is obtained for this new temperature, it will be found to lie on a line such as one of the dashed lines in Fig. 12. These lines are called instantaneous lines. They are roughly parallel to one another. These instantaneous lines are the only ones which truly represent the activity.

The *B* line is obtained by glowing at 1050°K, reducing the temperature to a lower value for a considerable time, applying the plate voltage and observing the emission at the instant the plate voltage is applied. If the plate voltage is kept on, the current will again end on the *C* line.

With such a diagram of steady value and instantaneous lines it is possible to predict the time changes that will occur in a coated filament under any set of circumstances provided it is known where the state of the filament can be represented by a point on this diagram. For example, suppose we know that the state of a filament is such as to be represented by a point d_1 on the

D line at a low temperature T_1. Suppose we now wish to know what happens if the temperature is increased to T_2 and (a) no current is drawn or (b) current is drawn. In the first case the activity will be given by i_2 in Fig. 12 and will increase to d_2. In the second case the current will decrease from i_2 to c_2.

All the lines represented in Fig. 12 are for a single plate potential of 60 volts. For a different plate potential an entirely new set of curves would hold. If the filament is given a severe treatment a complete new set of lines results.

We shall next consider uncombined filaments. Fig. 13 shows two sets of power emission lines which show the type of time changes that occurred in an uncombined strontium oxide filament before it was broken down (lines with subscript 1) and after it was partially broken down (lines with subscript 2). The dashed line A_1 represents the instantaneous emission current obtained at various temperatures after the filament had been thoroughly glowed at 1200°K. At any temperature below about 950°K the emission current increased with time, came to a peak value which is represented by a point on the P_1 line at that temperature, and then decreased to a steady value represented by a point on the B_1 line. Above about 950°K the current no longer passed through a peak but attained a steady value which again fell on the B_1 line.

After large currents had been drawn from the filament for considerable periods of time so that the filament was partially broken down, the analogous instantaneous line A_2, the peak line P_2, and the steady value line B_2 were obtained. At a given temperature the instantaneous activity had increased one hundred to five hundred-fold. The angles between A_2 and P_2, and A_2 and B_2 were now considerably smaller than the analogous angles in the preceding case. The point at which the peak phenomena disappeared was shifted to lower currents and to lower temperatures. These and other sets of such lines for different degrees of breakdown show that the peak phenomena become less pronounced and are shifted to lower temperatures as the breakdown process continues. The angle between the instantaneous line and the steady value drawing current line decreases as the breakdown process increases. These deductions fit in well with Fig. 12 for which no peak phenomena were observed and for which the angle between the instantaneous line A and the steady value glowing line C is very small.

From the discussions which have been given in preceding sections it follows that the only lines whose slopes may properly be used to obtain work functions are the instantaneous lines. If the data represented by the A_1 and A_2 lines in Fig. 13 and the A line in Fig 12 are replotted in the customary way, i.e., $\log i{-}2 \log T$ vs. $1/T$, straight lines are obtained whose slopes yield work functions of 1.8, 1.3, and 0.53 volts respectively. Since it is questionable that the work function of a composite surface is independent of the temperature, no great significance is to be put on any work functions determined in this manner. As far as they go, however, the values for the work functions are quite satisfactory, since the value 0.53 volts is for a filament which was in an unusually active condition. It might be well to point out that if work functions had been based on the steady value drawing current lines there might have been an error by more than a factor of two.

From the discussion of time changes given in preceding sections, the reader can appreciate the significance of these various lines. Their complete interpretation must be left until an even more exhaustive study has been made.

SUMMARY

The activity of a coated filament depends upon the surface concentration of metallic barium, the surface concentration of oxygen, on the relative positions of the barium and oxygen, and on the composition of the underlying oxide. Barium can be deposited on the surface either by evaporation from an outside source, which may be another coated filament, or else by electrolysis due to sending electrons into the filament from an outside source. In either case the barium on the barium oxide acts similar to barium on tungsten: as the amount of barium increases, the log of the emission at a given temperature increases rapidly at first and then more and more slowly until it passes through an optimum value beyond which it decreases. Oxygen may also be deposited on the surface either by evaporation or by electrolysis due to drawing current from the filament itself. The effect of this oxygen on the activity is quite complex: in general it is similar to the effect of oxygen in the case of barium on oxygen on tungsten; if the oxygen is between the surface layer of barium and the oxide, it increases the activity while if the oxygen is above the surface layer of barium it decreases the activity. Both barium and oxygen diffuse quite readily from the surface into the oxide and vice versa. The rate of diffusion increases rapidly with the temperature and with the concentration gradient near the surface. When current is sent into the oxide or drawn from the oxide most of it is carried by electrons, but a small portion is carried by oxygen and barium ions. The ratio of ion current to total current depends upon the temperature, the composition of the oxide, and in the case of drawing current on the plate potential. The complex changes in activity that occur in time when the filament is treated in various ways can best be described in terms of various "power-emission" or equivalent Richardson lines, namely, instantaneous lines, steady value glowing lines, steady value drawing current lines, and peak lines. These complex time changes can in a general way be interpreted in terms of the proposed theory. Some of the features require further study.

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