

PHENOMENA IN OXIDE COATED FILAMENTS II.  
ORIGIN OF ENHANCED EMISSION

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## ABSTRACT

Various theories have been advanced regarding the mechanism of emission of electrons from oxide coated filaments. These theories postulate that; (1) the active layer is (a) at the outer oxide surface, (b) at the core-oxide interface; (2) the thermionic electrons come from (a) the adsorbed barium, (b) the oxide just underneath the adsorbed layer; (3) the current is carried through the oxide coating by (a) an entirely electrolytic process, (b) thermionic electrons which come from the core, diffuse through the pores of the coating and form a space charge therein, (c) electrolytic conduction through the oxide crystals and thermionic conduction between crystals, (d) electronic conduction, a small portion being carried by ions. A number of experiments were designed to test these various hypotheses. These experiments show that; (1) When barium is brought to the outer surface of the oxide, either by electrolysis or evaporation from an external source, the emission increases at first, passes through a maximum and then decreases. This change in activity is similar to that for barium on tungsten. (2) When oxygen is brought to the surface of the oxide of an activated filament, the activity decreases rapidly at first and then more slowly. (3) In these two respects, a filament with a core made of an alloy called "Konel" and consisting of nickel, cobalt, iron and titanium acts just like filaments with other cores. (4) When the oxide was stripped from a Konel core filament, the activity decreased by a factor of 6000. (5) The emission-limited current is independent of the area of the core provided that the area of the outer oxide surface remains constant. (6) The conductivity of the oxide varies with the time of sending current through the oxide. (7) The conduction current in the oxide obeys Ohm's law and does not saturate even though its value is hundreds of times larger than the saturated emission. (8) The oxide acquires a positive potential with respect to the core regardless of whether the space current is limited by space charge or by emission. This potential varies linearly with the space current drawn to the plate and is of the order of a few tenths of a volt. (9) The emission for the optimum amount of barium on the oxide surface depends upon the previous treatment of the oxide. From these results we conclude that; (1) The active layer is at the outer oxide surface. The activity depends on the concentration of barium and oxygen on this surface and also upon the amount of metallic barium dispersed through the oxide. The core material does not directly affect the emission but it does greatly affect the ease with which free barium is produced by heat treatment or electrolysis. (2) The thermionic electrons originate in the oxide just underneath the adsorbed barium. (3) Most of the current through the oxide is conducted by electrons, a small portion being carried by barium and oxygen ions.

## INTRODUCTION

IN 1929 one of us proposed a comprehensive theory to account for the complex phenomena observed in oxide coated filaments.<sup>1</sup> The essential points of this theory were: The activity depends upon the concentration of barium<sup>2</sup>

<sup>1</sup> Becker, Phys. Rev. **34**, 1323-1351 (1929).

<sup>2</sup> Throughout this article the word "barium" will be used for barium and / or strontium and / or calcium.

and oxygen on the surface of the oxide and on the composition of the coating. Both barium and oxygen diffuse quite readily from the surface into the oxide and vice versa. When current passes through the oxide most of it is carried by electrons, but a small portion is carried by oxygen and barium ions.

Since that time we have enlarged or extended the theory or made it more explicit. Others too have proposed theories which, in some respects, conflict with ours. Insofar as these extensions or conflicts deal with the production of the barium or the conduction of current through the oxide, they have been dealt with elsewhere.<sup>3</sup> The present article will deal with the question: Where do the thermionic electrons originate?

It has been quite generally held that these electrons come from the region near the outer oxide surface. Recently, however, in two important papers it has been proposed that the electron space current is or may be limited by the emission from the metallic core surface of the filament. Lowry<sup>4</sup> states that, "the source of emission is assumed to be a layer of metallic barium occluded on the surface of the base metal or alloyed with it". He further postulates that "the electrons emitted from this composite surface must diffuse through the pores of the coating". Reimann and Murgoci<sup>5</sup> believe that electrons are thermionically emitted from the core to an adjoining oxide crystal and from one oxide crystal to the next. In each crystal the current is carried exclusively by barium ions. The barium atoms adsorbed on the surface of the outermost oxide crystals emit the electrons which pass to the plate. They conclude that the observed current may be limited by "whichever of the two systems (core or oxide surface) has the lesser emissivity".

Koller,<sup>6</sup> Rothe,<sup>7</sup> Detels,<sup>8</sup> Espe,<sup>9</sup> Becker,<sup>1</sup> Schottky,<sup>10</sup> Gehrts,<sup>11</sup> Huxford<sup>12</sup> and others believe that the emission depends upon the concentration of barium on or very near the surface of the oxide and that the core surface does not determine or limit the emission. There are differences of opinion, however, concerning the origin of the thermions near the oxide surface. Some believe that the thermions come from barium atoms adsorbed on the oxide; that the activity is proportional to the concentration of this adsorbed barium; and that the work function is the same for all appreciable concentrations of barium. Others believe that the thermions originate in the oxide just beneath the surface and that the adsorbed barium makes it easier for them to escape from the surface. On this view the work function depends on the concentration of barium and the activity is not directly proportional to this concentration.

In order to decide between these various theories we have designed and

<sup>3</sup> Becker, *Trans. Amer. Electrochem. Soc.* **59**, 207-220 (1931).

<sup>4</sup> Lowry, *Phys. Rev.* **35**, 1367-1378 (1930).

<sup>5</sup> Reimann and Murgoci, *Phil. Mag.* **9**, 440-464 (1930).

<sup>6</sup> Koller, *Phys. Rev.* **25**, 671-676 (1925).

<sup>7</sup> Rothe, *Zeits. f. Physik* **36**, 737-758 (1926).

<sup>8</sup> Detels, *Jahrb. d. drahtl. Telegr. u. Teleph.* **30**, 10-14 and 52-60 (1927).

<sup>9</sup> Espe, *Zeits. f. techn. Physik* **10**, 489-495 (1929).

<sup>10</sup> Schottky, See *Wien-Harms Handbuch der Physik*, Vol. XIII, part 2.

<sup>11</sup> Gehrts, *Zeits. f. techn. Physik* **11**, 246-253 (1930).

<sup>12</sup> Huxford, *Phys. Rev.* **38**, 379-395 (1931).

performed a number of crucial tests. These were so chosen that the predictions based on one theory were distinctly different from those predicted by some other theory. The first group of tests was designed to decide between the core-surface or the oxide-surface theory; the second group was intended to decide whether the electrons come from the adsorbed atoms or the underlying oxide. We shall describe these tests and discuss the deductions based on them and on tests described by others.

The experiments were conducted in radically different types of tubes. A description of each tube will be given in connection with the particular tests performed with it.

All of the tubes were evacuated on a four-stage mercury diffusion pump. During the pumping, which usually consumed two or three days, a tube was baked, the metal parts were outgassed and the tube was rebaked. The filaments were glowed at suitable temperatures until they were completely outgassed. The tubes were sealed from the pumps with the metal parts quite hot while the pressure was about  $1 \times 10^{-6}$  mm of Hg. All of the tubes contained auxiliary thoriated tungsten filaments which were used as "clean-up filaments" for several days or weeks after seal-off, until the pressure was about  $3 \times 10^{-8}$  mm of Hg or less, even when the oxide coated filaments were glowing.

The oxide coated filaments consisted of a mixture of barium and strontium carbonates, in a suitable suspension, coated on a metallic core. The carbonates were decomposed to the oxides by glowing while the tubes were on the pumps.

#### THE EFFECT OF BARIUM ON THE EMISSION

In a previous article<sup>1</sup> it was shown that the activity of an oxide coated filament changes as barium is put onto the outer oxide surface either by evaporation from an external source or by electrolysis of the oxide itself. From such results the conclusion was drawn that the source of the enhanced emission was at the outer oxide surface or within the oxide very close to the surface. The experiments were conducted with filaments having platinum and nickel cores. It has been reported<sup>4</sup> that oxide coated filaments having cores made of an alloy called "Konel" and consisting of nickel, cobalt, iron and titanium behave differently from filaments with other cores. It was therefore deemed advisable to repeat these experiments with a Konel core filament.

These experiments were conducted in a tube containing an oxide coated Konel filament and an auxiliary filament which could be used either as a source of electrons or as a source from which barium would evaporate under the proper conditions. A cross section of the tube showing the relative arrangement of filaments and plates is shown in Fig. 1.  $F_1$  and  $F_2$  are ribbon filaments mounted parallel to the plates  $P$ .  $F_1$  is an oxide coated Konel filament and  $F_2$  a barium-platinum alloy filament. The filaments  $F_3$  were of thoriated tungsten.  $S$  is a shield between  $F_1$  and  $F_2$  extending along their entire length. When it was desired to evaporate barium from  $F_2$  onto  $F_1$ , the shield could be removed into position  $S'$  by tilting the tube.

In these experiments, tests of the activity of the coated filament were made after subjecting the filament to various treatments. These treatments

consisted in: (1) Sending various amounts of current into the coated filament from the auxiliary filament  $F_2$ , (2) subsequent glowing of filament  $F_1$  at various temperatures, (3) evaporating various amounts of barium onto  $F_1$  from  $F_2$ , (4) subsequently glowing  $F_1$  at various temperatures.

The results are shown in Fig. 2 which is a plot of the emission current in amperes on log scale at a filament temperature of 500°K versus the time of subjecting the filament to the various treatments. The coated Konel filament was conditioned initially by glowing at a temperature of 1100°K until the emission reached an equilibrium value. Then a current of 450 microamperes was sent into the cold coated filament from the auxiliary filament  $F_2$ . After various intervals the current was stopped and the activity of the coated filament determined at a temperature of 500°K. The activities at these intervals are shown on the curve by the black dots. The activity increased at first until

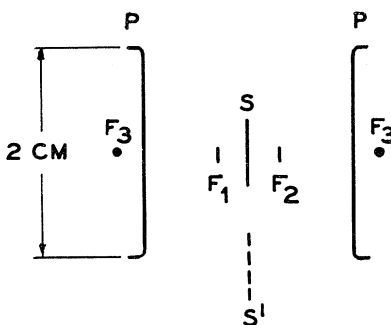


Fig. 1. Arrangement of plates and filaments in tube-152-S.

it reached an optimum value after which it decreased but at a slower and slower rate. A total of 7200 microampere minutes was sent into the coated filament.

The second treatment consisted in glowing the coated filament at 1040°K and later at 1100°K. The activity was again determined periodically at the testing temperature. The values of the activity thus obtained are shown on the curve by the first set of circles. The activity increased back to the optimum value and then decreased. The glowing at 1100°K caused the activity to fall rapidly to its equilibrium value.

The third treatment consisted in evaporating barium onto the surface of the cold coated filament. This was accomplished by removing the shield and glowing the auxiliary filament  $F_2$  at a suitable temperature. During this evaporation no current passed between the two filaments. At intervals the evaporation was stopped and the activity determined as in the previous experiments. The activities at the various times of evaporation are shown on the curve by the crosses. The activity increased initially until it reached an optimum value after which it decreased. An increase in the rate of evaporation from the auxiliary filament increased the rate at which the activity decreased.

The last treatment consisted in glowing the coated filament at 1040 and 1100°K as before. The activities at the various intervals of glowing are shown

by the second set of circles. The activity again increased to an optimum and then decreased to an equilibrium value.

Several auxiliary tests were made on this filament to show that the phenomena observed in Fig. 2 were caused directly by the treatment. The testing temperature of 500°K was sufficiently low that glowing or drawing testing currents at this temperature did not change the emission, regardless of the state of activation.

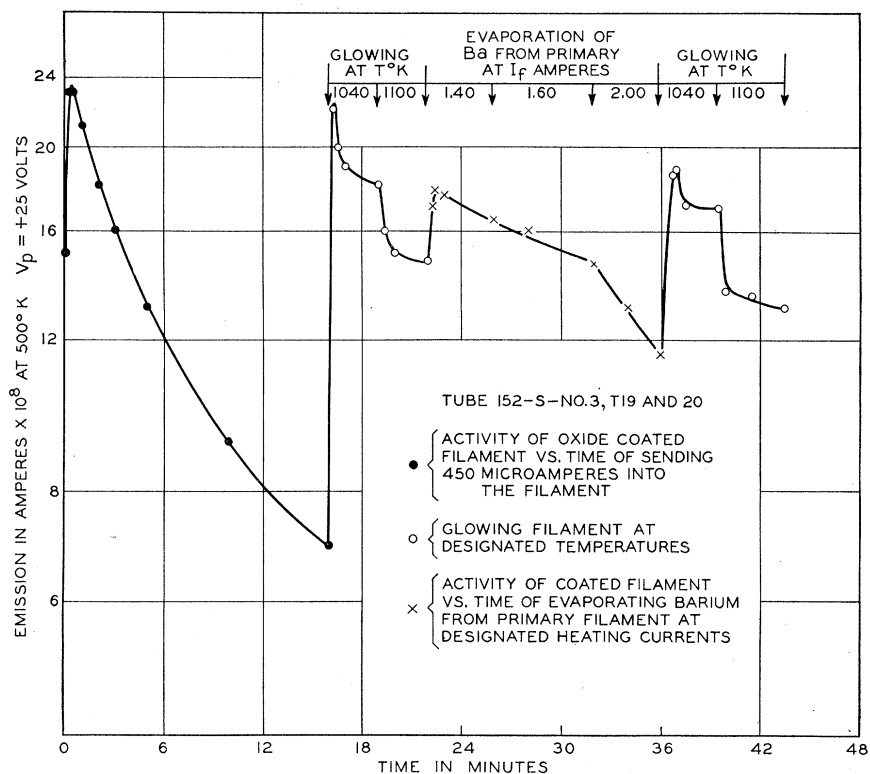


Fig. 2.

That the changes in emission, when electrons were sent into  $F_1$ , were due only to the action of the current entering the filament, was demonstrated in two ways. If the potentials of the various electrodes in the tube were arranged so that no electrons reached  $F_1$  even though electrons left  $F_2$ , the activity of  $F_1$  was not altered. In the second place, the change in activity of  $F_1$  was the same whether the shield was between  $F_1$  and  $F_2$  or not, provided only that the current into  $F_1$  was the same in the two cases. The insertion of the shield would prevent barium from reaching  $F_1$ , even if it did evaporate from  $F_2$ .

This last fact was demonstrated by inserting the shield when the temperature of  $F_2$  was such that barium did evaporate from it. In that case the activity of  $F_1$  was not affected until the shield was removed.

It should be noted that in order to obtain reproducible results when barium was evaporated onto the coated filament, it was necessary to have the pressure less than  $5 \times 10^{-8}$  mm of Hg. This is due to the fact that at higher pressures the rate of adsorption of gas atoms and molecules is appreciable. Such adsorbed gas will, of course, alter the activity. It was also necessary to have the platinum-barium alloy filament well conditioned in order that barium and only barium evaporated.

The results of the experiment shown in Fig. 2 can readily be interpreted on the view that the emission is dependent upon the amount of barium on barium oxide. When electrons are sent into an oxide coated filament, the direction of the electrolysis of the oxide is such that the barium ions travel toward the outer surface. Since the changes in emission noted in this experiment were caused by electrons entering the filament, we conclude that the emission changed as various amounts of barium were deposited on the oxide surface. As more and more barium was deposited on the surface the emission increased until it reached an optimum value, after which it decreased. Glowing the filament at 1040°K caused this excess of surface barium to diffuse into the interior of the oxide or to evaporate. The emission, therefore, increased back through the optimum value. Glowing at 1100°K caused the emission to decrease to its equilibrium activity on glowing at that temperature.

This interpretation is confirmed by the second part of this experiment in which barium was evaporated directly onto the oxide surface. The emission changed as the surface concentration of barium changed. As the amount of barium on the surface increased, the emission increased to the optimum value and then decreased just as in the previous case where barium was put on the surface by electrolysis. Subsequent glowing at 1040 and 1100°K again caused this barium to diffuse into the oxide or to evaporate. This in turn caused the emission to increase back to the optimum and then decrease to an equilibrium value.

The first two optima in Fig. 2 have the same value. From this we may conclude that the entire oxide surface was uniformly covered with barium. Presumably the electrons entered the coating from all directions and deposited barium uniformly over the entire surface. The optimum obtained by evaporation of barium onto the surface was less than these optima. The reason is that barium was evaporated onto only one side of the filament. Consequently, the emission from the back side of the ribbon remained constant while that from the front side increased to the optimum. The ratio of the first and third optima in Fig. 2 is of the proper magnitude to agree with this interpretation.

The last optimum emission on glowing at 1040°K was slightly higher than the optimum which just preceded it. After barium had been evaporated onto the ribbon, the front side was covered beyond the optimum while the back side was covered with less than the optimum amount of barium. The fourth optimum in Fig. 2 was slightly higher than the third because during the initial stages of glowing at 1040°K some of the barium from the front side migrated to the back side of the ribbon and increased the barium concentration there.

Thus far we have interpreted the changes in activity when current was

sent into the oxide coated filament in terms of the barium deposited at the outer oxide surface by electrolysis. The oxygen deposited near the core was assumed to have no effect on the activity. This assumption can be verified by comparing the results when the oxide was electrolyzed with those obtained when barium was evaporated onto the oxide surface. The third optimum in Fig. 2, when corrected for the fact that barium was evaporated onto only one side of the ribbon, is equal to the first optimum. Since oxygen was deposited near the core face in one case and not in the other we conclude that oxygen on the core face does not affect the activity.

Our observed changes in activity when barium was made to appear or to leave the surface of the oxide are qualitatively similar to those observed for barium on tungsten. They are strikingly different, however, in one respect. For barium on tungsten, the optimum activity is thousands of times greater than that for clean tungsten, while for the cases of barium on the oxide discussed above, the optimum activity is less than twice the initial activity. This dissimilarity is due to the fact that when an activated oxide filament is glowed at moderate temperatures, its surface is not freed from adsorbed barium. In fact, the surface in some cases may be nearly completely covered, as was shown in a previous paper.<sup>1</sup>

These results do not seem to be readily interpretable on the view that the emission is determined by the amount of barium on the core face. The testing temperature was so low that the barium could not have diffused into the oxide and increased the barium concentration at or near the core. The observed changes in emission were, therefore, not due to any change in the system at or near the core surface but must have been due to changes in barium concentration on the surface of the oxide.

#### THE EFFECT OF OXYGEN ON THE EMISSION

Whether the emission is determined by the core surface or oxide surface can also be tested by observing the effects of oxygen on the emission. It has been shown<sup>1</sup> that if oxygen is brought to the surface of an active oxide coated platinum-nickel core filament, the activity decreases. The effect is the same whether the oxygen is deposited by evaporation from an external source or whether it is produced by electrolysis of the oxide. From these experiments it follows that in active filaments with a platinum nickel core, the emission is determined by the outer oxide surface. We have used a Konel core filament in repeating the experiments in which oxygen is brought to the surface by electrolysis.

These experiments were performed in a tube of the same type as that used in studying the effect of barium on the emission and shown in Fig. 1. As emission-limited current was drawn from the coated filament to the plates, the activity decreased rapidly and then more and more slowly. This is illustrated in Fig. 3. Curve 1 shows how the emission current decreased as current was drawn to the plates at a temperature of 660°K and a plate potential of 100 volts. At intervals, during this drawing of current, the activity was tested at a lower temperature, 500°K. Curve 2 shows how the activity under the nor-

mal testing conditions decreased with the time that current was drawn at a temperature of 660°K. The activity at the testing temperature decreased by a factor of ten. The filament was then glowed at 770°K and the emission increased rapidly at first and then more and more slowly as shown by curve 3. The glowing temperature was finally raised to 900°K and the activity increased back to its normal value as shown by curve 4.

These results are very similar to those previously found with a platinum-nickel core filament as can be seen by comparing Fig. 3 of this paper with Fig. 10 of the previous paper.<sup>1</sup> From this it seems clear that the behavior of coated filaments with Konel cores is not essentially different from that in filaments with platinum-nickel or platinum-iridium core. In both cases the decrease in activity is due to oxygen on the surface. This means that the thermionic emission is determined by the condition of the outer oxide surface.

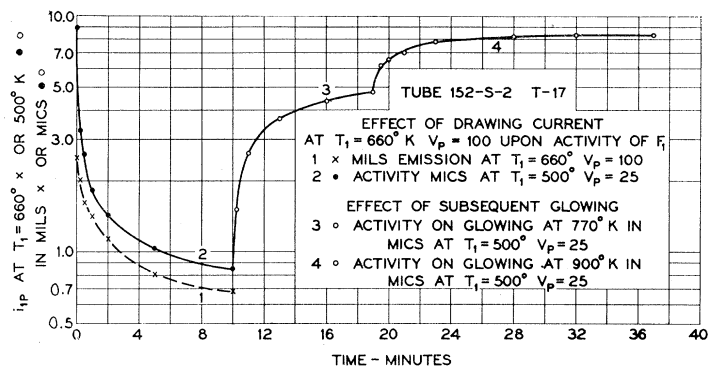


Fig. 3.

These time changes caused by the electrolytic deposition of oxygen are obtained most readily at moderate plate currents and moderate temperatures. However, in vacuum tubes operating normally, heavy currents are usually drawn from the filament to the plate at temperatures around 1050°K. Under these conditions the activity usually remains quite constant with the time of drawing current. There are two reasons for this: (1) The currents are usually limited by space charge and the proportion of current in the oxide carried by ions is very small.<sup>1</sup> (2) At this temperature the rates of diffusion of barium and oxygen in the oxide are high so that the oxygen and barium ions upon becoming neutralized at or near the outer oxide and core surfaces respectively diffuse quite rapidly back into the oxide.

#### EFFECT OF REMOVING OXIDE COATING

The next type of experiment was designed to make a test of the hypothesis that the enhanced emission is due to barium adsorbed on the core surface. On this view, if the oxide were removed from the core, the emission should be at least as great as before. The tube used for this test consisted of two parallel plates, in the center of which was placed an oxide coated filament with a



Konel core. The filament was in the form of a ribbon approximately 0.125 cm (50 mils) wide. The adherence of the coating to the core of this particular filament was exceptionally poor so that if the filament was subjected to a mechanical vibration or strain, the coating would completely peel off.

The experiment consisted in observing the activity before and after the coating was removed. The filament was activated initially by glowing. The activity of the coated filament on glowing for a number of hours at approximately 1050°K is shown by power-emission line *A* in Fig. 4. After this activity was observed, the filament was cooled to room temperature and the tube

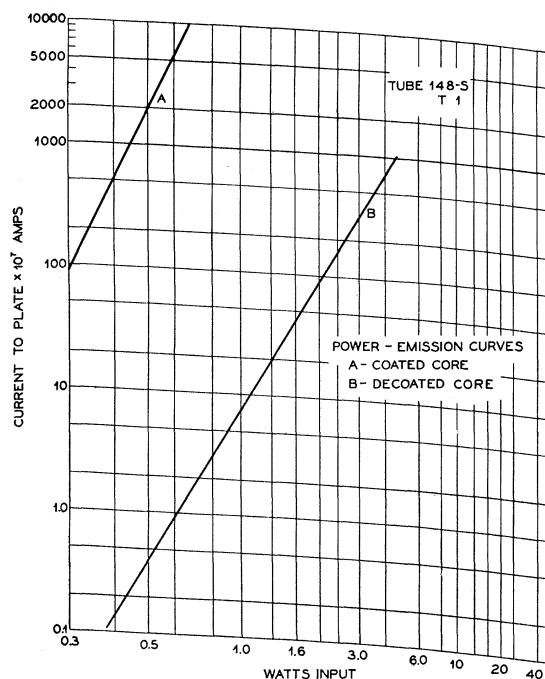


Fig. 4.

jarred. This caused all of the coating to fall off. The activity was again measured at low temperatures and is shown by power-emission line *B*. The activity decreased by a factor of about 6000. Subsequent glowing of the decoated core failed to change the emission appreciably. The decoated core was of a greyish appearance due to the usual oxidation of the core metal during the treatment of the filament.

Power-emission line *B* was taken at temperatures sufficiently low that barium could not have evaporated from the decoated core surface had it been there directly after the removal of the oxide. It is known that barium will not evaporate from a tungsten surface even at much higher temperatures than those used in determining line *B*.<sup>13</sup>

The results of this experiment can readily be interpreted on the view that

<sup>13</sup> Eglin, Phys. Rev. **31**, 1127 (1928).

the emission is dependent upon the amount of barium on barium oxide. The large decrease in emission was due to the loss of the oxide coating which carried the outer oxide surface of low work function with it.

The large decrease in emission is not in accord with the view that the emission is determined by the amount of barium adsorbed on the core face unless the assumption is made that the barium adsorbed on the core adheres more tenaciously to the oxide than to the core and that when the oxide and core are parted, the barium chooses to remain with the oxide. We know of no way of testing such an assumption. We do know that barium sticks tenaciously to both metallic and oxide surfaces. It seems quite probable, therefore, that some of the barium should have remained on the core. If the core had been

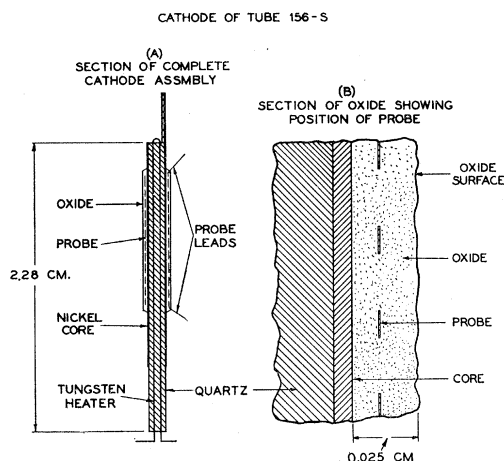


Fig. 5.

“active” when the coating was present it should have been partially “active” when the coating was removed and subsequent glowing at high temperatures should have changed the activity.

#### EFFECT OF CHANGING THE AREA OF SUPPOSED EMITTER

On the view that the electrons are emitted thermionically between core and coating, the current that reaches the plate may be limited by the number of electrons that are able to leave the core. If the area of the metallic core surface, from which the electrons are supposed to escape, could be reduced, the emission should be reduced proportionately. On the other hand, if the emission is limited by the external oxide surface, it should not change when the area of the core surface is changed.

Such an experiment was conducted in a tube containing an equipotential cathode cylinder coated with a mixture of barium and strontium oxide in which was embedded a metallic ribbon or probe completely insulated from the core. An enlarged cross-section of the cathode is shown in Fig. 5A. An indirectly heated cathode was employed, consisting of a tubular nickel core covering a quartz rod in which was a tungsten heater wire. The nickel core

was coated with a layer of oxide; then a  $0.0025 \times 0.0127$  cm ( $1 \times 5$  mil) nickel ribbon, which had previously been coated with a layer of oxide, was wound helically about the coated core and the whole coated over with a second coat of oxide. A much enlarged cross-section of the oxide showing the relative positions of core, nickel ribbon or probe and oxide, is shown in Fig. 5B. The area of one side of the probe is equal to about one-third of the area of the core. The cathode assembly shown in Fig. 5A was placed in the axis of three cylindrical anodes, 1.5 cm in diameter. The outside two cylinders are 0.8 cm and the central collector 0.6 cm long. Six thoriated tungsten filaments were placed outside of these collectors for use as clean-up filaments.

The experiments consisted in measuring the emission from the cathode to the plate when the negative terminal of the battery was connected to: (1) the core with the probe floating, (2) the probe with the core floating and, (3) both core and probe. The metallic surface areas are as 1, 2/3 and 5/3.

The results of this test are shown in Table I. The emission currents, when the negative terminal of the battery was connected to the core, probe, and core and probe together are given for several different temperatures. At any temperature, the emission currents in all three cases are practically equal.

TABLE I.

Temp. °K	Emission current in amps. with 40 volts applied between plate and		
	Core (Probe floating)	Probe (Core floating)	Core and probe
545	$4.85 \times 10^{-8}$	$4.78 \times 10^{-8}$	$4.80 \times 10^{-8}$
643	$3.06 \times 10^{-6}$	$2.84 \times 10^{-6}$	$2.98 \times 10^{-6}$
711	$2.42 \times 10^{-5}$	$2.14 \times 10^{-5}$	$2.31 \times 10^{-5}$

These results cannot be interpreted on the view that the electron current is limited by emission from the core. Since the current "emitted" from the core alone was equal to the current "emitted" from the probe alone, one would certainly expect the resultant emission, when the plate battery was connected to both core and probe, to be appreciably larger than the emission from either one alone. This was not verified as can readily be seen from the table.

On the other hand the results are to be expected on the view that the electrons are emitted thermionically from the external oxide surface. The emission was the same in all three cases simply because the area of the outer oxide surface was unchanged.

#### OXIDE CONDUCTIVITY

Reimann and Murgoci<sup>5</sup> have investigated the variation of the conduction current between two coated filaments, twisted together, with the potential. They found that the current varied linearly with the voltage at low current densities but sometimes showed incipient saturation at potentials of a few volts. They state that, "at current densities comparable with those in the coatings of oxide cathodes from which saturated thermionic space current is being taken, the current conducted through an oxide powder between two electrodes, embedded therein, also saturates". From this they conclude that

the conduction current in any individual oxide crystal obeys Ohm's law and that the current is carried by thermionic electrons between the various crystals and between core and oxide. At low current densities, the currents across the gaps are limited by space charge and most of the potential drop is across the oxide crystals. This accounts for the linear portion of their curves. At high current densities, the current is limited by thermionic emission in one or more gaps. This interpretation is the basis of their conclusion that there is a limitation of thermionic space current, "between the core metal and coating or within the coating itself".

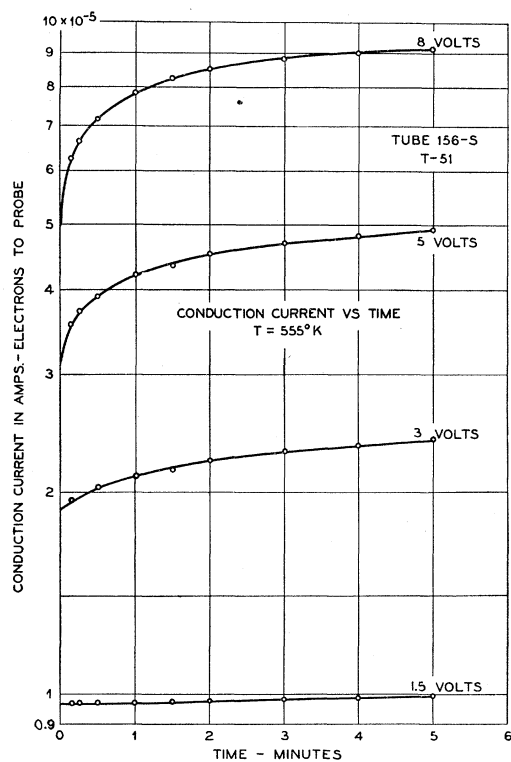


Fig. 6.

Due to the importance of this experiment, we have repeated their measurements with an improved design of tube. The tube contained the special equipotential cathode shown in Fig. 5. and was described in the preceding section.

The measurements consisted in noting the value of the conduction current when various potentials were applied between core and probe. It was found that as long as the currents and voltages were small, Ohm's law was obeyed, but if the applied potential was more than about one volt, the conduction current sometimes varied with the time. When the conduction current varied with the time, it always increased at a fast rate initially and then more and more slowly. In some cases it increased to an optimum value and

then decreased but did not fall below its initial value. The increase of conduction current with time is illustrated in Fig. 6. The conduction current on a logarithmic scale is plotted against the time that electrons were flowing from the core to probe at a temperature of 555°K. Four curves are shown for potentials between the core and probe of 1.5, 3, 5 and 8 volts. After each of these curves, the cathode was glowed for ten minutes at 555°K with no potentials applied. The curves were reproducible, showing that this glowing was sufficient to bring the oxide back to its initial condition. The conduction current always increased with time until at the end of five minutes it had reached an almost constant value. The phenomenon is attributed to an increase in oxide conductivity due to an accumulation of the products of electrolysis in the oxide. A more detailed study of this phenomenon is now in progress.

A current voltage curve can be obtained from the data of Fig. 6. Such a curve is shown in Fig. 7. Curve *A* was obtained by plotting the initial values of

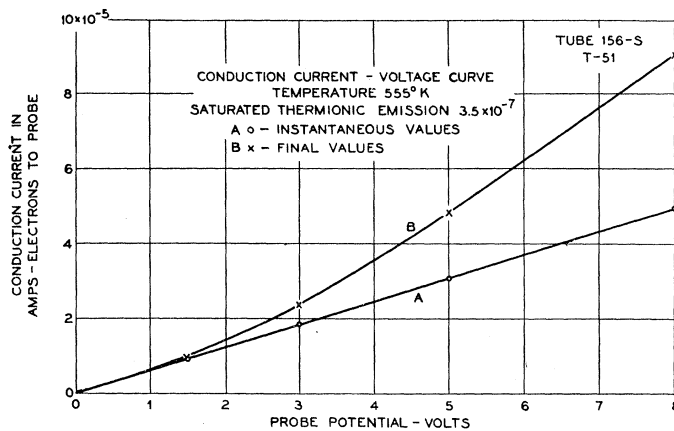


Fig. 7.

the conduction current against the applied potential. The points form a good straight line indicating that the oxide obeys Ohm's law. The final values of conduction current gave curve *B* which is concave toward the current axis. There is no indication of current saturation as reported by Reimann and Murgoci even though the current density at the highest potential is 300 times larger than the total saturated thermionic emission at this temperature. For these cathodes there can be no limitation of thermionic space current at the core face or in the oxide.

This particular test has been made on three cathodes with the same result. Furthermore we have never found a case in a large number of different types of coated filaments in which the behavior indicated such a limitation of thermionic current at the core surface. We therefore believe that the reported deviations from linearity may be attributed to changes in conductivity with time or to polarization since we have found the shape of our current voltage curves to be affected by these factors. It may also be that two filaments twisted together actually do form a gap in the oxide and that the current is limited at this gap.

## POTENTIAL DISTRIBUTION IN THE OXIDE

By means of the probe it is possible to test whether the electrons are emitted thermionically from the core and then drift through the pores of the oxide where they form a pseudo space charge. On this view the probe should sometimes be negative with respect to the core and the probe potential should not vary linearly with the current emitted to the plate. On the other hand, if the electrons are emitted thermionically from the outer oxide surface and if they

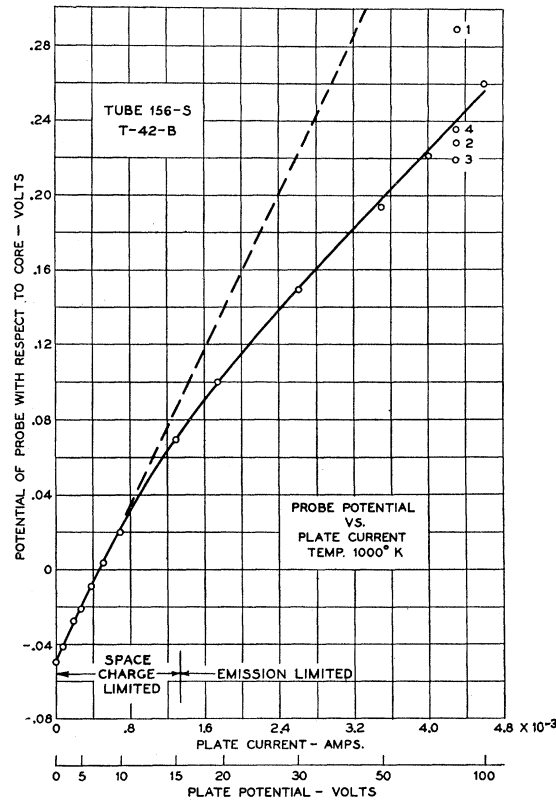


Fig. 8.

pass through the oxide as they would through a metal of high resistivity, the probe should always be positive with respect to the core and the probe potential should be directly proportional to the current through the oxide. Furthermore the ratio of the probe potential to the plate current should give the resistance of the oxide between the core and probe. The value of this resistance should agree with that determined in the conductivity measurements described above.

In the experiments to differentiate between these views, the potential of the probe in the oxide was measured as current was drawn from the core to the plate. A null method was used in measuring the probe potential. The results are illustrated in Fig. 8, which is a plot of the potential of the probe with re-

spect to the core versus the current to the plate in amperes at a temperature of  $1000^{\circ}\text{K}$ . The current to the plate was varied by changing the plate potential. The values of plate potential are indicated in Fig. 8 below the current values. The current was limited by space charge up to approximately 1.2 milliamperes. When the current was limited by emission, the current varied with the plate potential because of the characteristic poor saturation of these oxide cathodes.

These data show that the oxide is positive, regardless of whether the current reaching the plate is limited by space charge or by emission, as was predicted on the basis of our theory. However, the observed curve differs from the predicted in two respects.

In the first place the curve does not pass through the origin. When the plate current is zero, the probe has a negative potential with respect to the core. Since there is a constant flow of energy across the oxide, there must exist a temperature difference between the core and probe. The intercept, therefore, measures the thermal e.m.f. generated by the two nickel-barium oxide junctions at the two temperatures. The temperature difference is estimated to be something like 20 degrees. All of our conduction current voltage curves show this intercept. It does not appear in Fig. 7, however, due to the low temperature and the large voltage range plotted.

That the intercept is due to a thermal e.m.f. was demonstrated in the following manner: The core and probe were connected together through a variable resistance and a galvanometer. The current indicated by the galvanometer was changed by varying the external resistance. A plot was made of the reciprocal of the current versus the external resistance. The plot gave a straight line relation whose slope was equal to the floating probe potential at this temperature. Furthermore, the oxide resistance, as determined from this plot, agrees with the resistance determined from the slope of a current voltage curve at this temperature. This means that the core-oxide-probe system acts just like a source of e.m.f. with a definite internal resistance. The value of the e.m.f. or resistance varies with the temperature. It was found that the intercept of Fig. 8 varied linearly with the power input to the cathode as is to be expected if the temperature difference between any two points in a medium conducting heat is directly proportional to the rate at which energy flows through the medium.

The second deviation from the predictions is the fact that the curve in Fig. 8 is linear only in the region which is well defined by space charge. Over the portion of the curve in which the current is limited by emission, the potential increases more slowly than the current. This is due to the fact that the probe potential varies with the time and the points shown on the curve represent equilibrium values. Thus, when the plate current was suddenly changed from a low value to 4.3 milliamperes, by raising and maintaining the plate potential to approximately 80 volts, the probe potential changed rapidly with time, as illustrated by points 1, 2, 3 and 4, which were taken 5, 25, 80 and 300 seconds respectively after the plate current was increased.

This phenomenon is the same as that observed when conduction current

is drawn between core and probe and which was described above. If instantaneous values of probe potential had been taken, the straight dashed line would have been obtained. The slope of this line represents the resistance of the oxide between the core and a point in the plane of the probe.

If this interpretation is correct, the resistance as thus determined should be somewhat less than the resistance obtained from the initial line of a conduction current-voltage curve at the same temperature. From Fig. 8 the oxide-resistance is 105 ohms. The resistance determined from the slope of a conduction current voltage curve at the same temperature is 268 ohms. The ratio of these resistances is 2.65. At a temperature of 756°K, the resistance obtained from the probe potential plate current curve is  $0.54 \times 10^4$  ohms and the resistance determined from the slope of the conduction current-voltage curve is  $1.15 \times 10^4$  ohms. The ratio between these resistances is 2.12. Since the ratios of the cross-sections of the current paths in the two types of curves is somewhat greater than 1 and somewhat less than 3, it is to be expected that the ratio of the resistances would be somewhere between these values. The observed ratios 2.65 and 2.12 are entirely reasonable. Furthermore, the plate current-probe potential curves are similar to the conduction current-voltage curves as regards their deviation from linearity. This deviation from linearity occurs at the same potential difference between core and probe for the two curves. The magnitude of the deviation at any probe potential is approximately the same in the two cases.

These results fully confirm the prediction that the potential of a point in the oxide with respect to the core should be positive and should be directly proportional to the current through the oxide. It is therefore reasonably certain that the electrons pass through the oxide as they would through a metal of a high resistivity and that they do not become occluded on the oxide particles and thus set up a pseudo space charge.

The conclusion that the active layer is on the oxide surface and that the current is not carried thermionically between core and coating is based thus far on tests in special experimental tubes. It can be extended to numerous other tubes by a consideration of the potential distribution between two insulated bodies both of which are thermionic emitters. Let us assume that the electrons are transferred thermionically from the core to the coating and then reemitted thermionically from the coating to the plate. Let us further assume that the electron emissivity of the core is considerably less than that of the coating. Before any potential is applied to the plate, the potential of the oxide will differ from that of the core by a potential equal to the contact potential difference at the core-oxide interface. At the instant when a positive plate potential is applied, the coating will give up more electrons to the plate than it receives from the core. Consequently the coating will become positively charged with respect to the core and the potential difference between coating and plate will decrease. As long as this potential difference between coating and plate is sufficient to keep the current from the coating saturated, the electron emission from the coating will exceed that received by the coating, and the coating will become more and more positively charged. This process



will continue until the current from the coating is limited by space charge and is just equal to the emission limited current from the core to the coating. When this steady state is reached, an appreciable part if not most of the potential difference applied between core and plate will be used up between the core and the coating. Consequently, when the space current is limited by emission; (1) the potential of a probe embedded in the oxide should be an appreciable fraction of the applied potential; (2) an appreciable part if not the major part of the energy dissipated in the tube should be dissipated in the coating, which should consequently get very hot.

These predictions are not confirmed by experiment. The data for Fig. 8 show that the probe potential is only about 0.3 volt even when the plate potential is 100 volts and even this 0.3 volt is to be ascribed to an  $iR$  drop rather than to a potential difference across the core-oxide interface. Furthermore, it is a well-known fact that in commercial tubes, a negligible part of the energy represented by the product of the space current and the applied plate potential is dissipated in the filament. It is only in unusual filaments with very thick, shaggy coatings that any appreciable part of the applied potential is used up in the oxide and in this case the resistance of the coating is sufficient to account for the energy dissipated in the filament. These facts make it appear improbable that the emission is ever limited by the core in ordinary oxide coated filaments.

#### DO THE ELECTRONS COME FROM THE ADSORBED BARIUM ATOMS OR FROM THE UNDERLYING OXIDE?

While it is obviously impossible to observe directly whether the emitted electrons come from the adsorbed barium or from the underlying oxide, nevertheless experiment can indirectly decide between these two views. The predictions made on these two views are quite distinct and can be tested by experiments.

If the thermions come from the adsorbed barium, the activity or emission current at a fixed temperature should be directly proportional to the number of monatomically adsorbed atoms and should increase steadily from a low value characteristic of a bare surface to a value characteristic of solid barium. On the other hand if the electrons come from the underlying oxide and if the barium is ionized and thus helps the electrons escape, one might reasonably expect the activity to increase at a rate which is much more than proportional to the concentration of adsorbed barium and that it might reasonably reach an optimum value for a monatomic layer before it decreases to its value characteristic of solid barium. Of course, eventually as the concentration of barium increases, the electrons must originate in the barium.

The experiments described above and in previous publications in which barium was deposited on the oxide surface either by electrolysis or by evaporation from an outside source, decidedly favor the second hypothesis and definitely contradict the predictions of the first hypothesis.

The behavior of barium on the oxides is strikingly similar to that of barium on tungsten. In both cases as the surface concentration increases  $\log i$

increases rapidly at first then more and more slowly, passes through an optimum and then decreases to approach the value for solid barium; when the surface concentration is subsequently decreased,  $\log i$  again increases to the same optimum and then decreases toward its original value. This striking similarity in behavior points to a similarity in the mechanism of emission in the two cases.

For a layer of barium or other electropositive elements adsorbed on tungsten, it is generally held that at least some of the adsorbed barium is ionized and that the emitted electrons come from the underlying tungsten rather than from the adsorbed barium. On this adion grid theory one can readily explain: (1) Why the work function decreases,<sup>14</sup> passes through a minimum and then increases,<sup>15</sup> (2) why the contact potential changes correspondingly,<sup>14</sup> (3) why the current voltage curves saturate poorly if the surface is not uniformly covered,<sup>16</sup> (4) why the barium sticks to the tungsten at relatively high temperatures,<sup>15</sup> (5) why the adsorbed elements sometimes come off as positive ions,<sup>14</sup> (6) why the rate of positive ion emission decreases as the surface concentration increases.<sup>14</sup>

Because this adion grid theory is capable of interpreting these experimental facts we believe that for one or perhaps even two layers of barium the emitted electrons come from the tungsten or oxide rather than from the barium.

There is one aspect in which barium on the oxides differs from barium on tungsten. In tungsten the number of "free" electrons or those available for emission is fixed; in the oxides this number probably increases by large factors as the amount of barium dispersed through the oxide increases. This view is based on the observation that the conductivity of oxides increases by large factors when the amount of free metal dispersed in the oxide increases. Presumably the electrons that take part in the conduction are also "free" to leave the surface of the oxide if they have sufficient kinetic energy when close enough to the surface. Consequently it is to be expected that the emission will depend not only on the amount of barium on the surface but also on the amount dispersed through the oxide. The barium on the surface makes it easier for each electron to leave the surface: It decreases the work function  $\phi$  in Richardson's equation,  $i = AT^2 \epsilon^{-\phi/kT}$ . The barium dispersed through the oxide increases the number of electrons that approach the surface: It increases the "A" in Richardson's equation.

We arrive at this view partly as a result of the following experiment. In the tube described in Fig. 1, the cathode was glowed at 1040°K until its activity as tested at 500°K reached a steady and reproducible value. A measured electron current was then sent into the cold oxide coating from an external filament for a measured time. The activity of the oxide filament as tested at 500°K was determined periodically. It was found that the activity increased, passed through an optimum and then decreased. Following this treatment,

<sup>14</sup> Becker, *Trans. Amer. Electrochem. Soc.* **55**, 153-175 (1929).

<sup>15</sup> Becker, *Bell Laboratories Record* **9**, 54-58, Oct. 1930.

<sup>16</sup> Becker, *Phys. Rev.* **35**, 1431 (1930).

the cathode was glowed at 1040°K while its activity at 500°K was again tested periodically. It was found that the activity increased at first, came to an optimum, which differed slightly from the preceding optimum, and then decreased until it approached a steady value. This steady value was greater than the preceding steady value on glowing at 1040°K. Electrons were then again sent into the oxide until the activity passed through an optimum and decreased. This treatment was again followed by a glowing treatment. Both processes were repeated again and again.

Fig. 9 shows some of the results. The various activities are plotted as a function of the total number of milliampere minutes (m.a.m.) of current sent into the oxide cathode. At any value of m.a.m. there are, in general, four characteristic activities shown in the figure. The first set of points do not

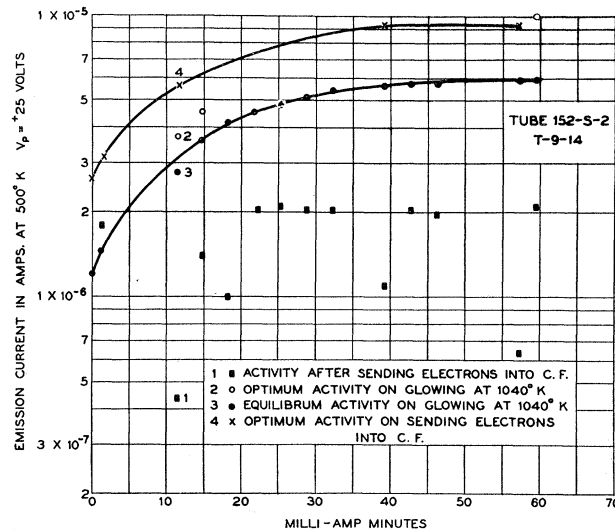


Fig. 9.

and should not form a smooth curve since the m.a.m. between successive glowings at 1040°K was irregular. If the interval between two successive glowings is unusually long, the initial activity is unusually low as it should be. The other sets of points form smooth curves as they should. The most important curve is the uppermost one for the optima on sending electrons into the oxide since each point represents the emission when the surface is covered with a monatomic layer of barium. This confirms the previously known fact, that the concentration of barium on the surface is not the only factor determining the activity.

We interpret this experiment as follows: After the initial glowing at 1040°K the concentrations of barium in the oxide and on the surface had reached a steady state. When electrons were sent into the oxide, oxygen was deposited on the core while barium was brought to the surface by electrolysis. The oxygen combined with the core since it is well known that a Konel core is readily oxidized. When the concentration of barium on the sur-

face reached a monatomic layer, the activity had an optimum value. We estimate that as the electrolysis continued in some cases several layers of barium were deposited on the surface. During the glowing at 1040°K this barium diffused back into the oxide and thus increased the concentration of barium dispersed through the oxide. After each treatment this concentration in the oxide was greater than after the preceding treatment. This is the reason why the optima and the steady value glowing curves increased with the m.a.m.

This experiment seems to us to be a crucial test between the two hypotheses; (1) that the electrons originate in the adsorbed barium itself, (2) they originate in the oxide underneath the adsorbed barium. On the first hypothesis it is difficult or impossible to see why there should be any optimum and why the optima should depend on the treatments to which the oxide was subjected. On the other hand, the second hypothesis is able to explain readily the observed facts.

#### THE RÔLE OF THE CORE METAL

In this laboratory it has long been recognized that the nature of the core material has a very great influence on the activities that can be attained and the ease with which they can be attained. King<sup>17</sup> has shown that the average electron emissivity of a number of "combined" coated filaments with platinum-nickel core was higher than the emissivity of similar coatings on platinum-iridium cores. More recently Lowry<sup>4</sup> has shown that uncombined coated filaments with Konel metal cores were better electron emitters than some coated filaments with platinum cores. The emission from oxide coated nickel is also usually much better than from oxide coated platinum. According to Beese,<sup>18</sup> if 0.1 percent of barium is alloyed with the core, the easily attainable activity is appreciably improved.

The influence of the core material on the easily attainable activities is thus a well established fact. It has usually been assumed that this influence is an indirect one. Recently Lowry<sup>4</sup> has expressed the belief that the core material directly affects the activity. As a result he, "assumes that the source of the emission is the composite layer formed by occlusion of alkaline earth metal on the surface of the core". He admits however, "that no crucial tests of this explanation have been offered except that of showing the pronounced influence of the core metal". The experiments described above constitute such a crucial test since they show that the activity is determined by the outer oxide surface. It is well known that thermionic properties are directly affected by only a few atomic layers near the surface. It is also well known that the oxide coating is thousands of layers deep. Consequently the effect of the core material must be an indirect one.

The ways in which the core material may indirectly affect the activity are numerous. Anything which increases the concentration of barium adsorbed on the surface of the oxide or dispersed through the oxide, or anything which changes the composition or physical structure of the oxide will affect the ac-

<sup>17</sup> King, Bell Tech. Jrl. **2**, 31-100 (1923).

<sup>18</sup> Beese, Phys. Rev. **36**, 1309-1313 (1930).

tivity. The oxide very likely reacts chemically with some core constituents to form metallic barium some of which reaches the surface by diffusion. Carbon which is frequently present in cores as an impurity almost certainly reacts with the oxides. In some cases certain core materials, nickel for example, may be dispersed through the oxides. Such dispersed materials change the conductivity of the oxide and the ease with which electrolytic decomposition takes place. It is quite likely that such impurities in the oxide affect the crystal size of the oxide and thus influence diffusion, adsorption, and electrolytic phenomena which in turn affect the activity. If the core is purposely made to contain metallic barium, this barium will diffuse through the oxide and become adsorbed on the surface. The core material may also influence the ease with which the carbonates are decomposed to the oxides when the filament is first heated. Finally, the core material certainly affects the composition of the compounds which are formed when oxide filaments are heated in air to make "combined" filaments. The nature of these compounds and the products of their decomposition when the filament is heated in a vacuum, certainly affects the activity. In these and numerous other cases the core affects the activity in a round-about way rather than directly.

#### CONCLUSIONS

From these experimental results we conclude that: (1) The active layer is at the outer oxide surface.<sup>19</sup> The activity depends upon the concentration of barium and oxygen on this surface and also upon the amount of metallic barium dispersed through the oxide. The core material does not directly affect the emission but it does greatly affect the ease with which free barium is produced by heat treatment or electrolysis. (2) The thermionic electrons originate in the oxide just underneath the adsorbed barium. (3) Most of the current through the oxide is conducted by electrons, a small portion being carried by barium and oxygen ions.

<sup>19</sup> Huxford (Phys. Rev. **38**, 379-395 (1931)) comes to this same conclusion as a result of his work on the photoelectric emission from oxide cathodes.