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Thermionic Emission of Thin Films of Alkaline Earth Oxide Deposited by Evaporation

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Monomolecular films of BaO or SrO were deposited by evaporation on clean tungsten or molybdenum surfaces with precautions to eliminate effects caused by excess metal of the oxide or by heating. Thermionic emissions of the same order of magnitude as from commercial oxide cathodes have been obtained from these systems. The results can be explained qualitatively by considering the adsorbed molecules as oriented dipoles. Although the results may suggest a possible mechanism for a portion of the emission from thick oxide cathodes, there are serious obstacles against such thin film phenomena as a complete explanation.

MANY authors have discussed thermionic emission from thin films of electropositive metals deposited on either clean or oxidized metallic supports, such as tungsten. Others have investigated the oxide cathode, a much more complex system. Only two authors seem to have investigated thin films of alkaline earth oxide on clean support metals—a system intermediate in complexity between the first two. Of these, Davisson and Pidgeon[1] found that a tungsten ribbon was activated by material evaporated from a neighboring oxide-coated cathode. Hull[2,3] found that molybdenum, after receiving material evaporated from a mixture of BaO and Al_2O_3 in a porous molybdenum stocking, became a very satisfactory cathode for thyratrons as a result of this evaporated deposit. For reasons not given, both papers definitely attribute the activation to BaO, rather than to the barium metal, which, at least in Hull's work, certainly[4] evaporated with the BaO.

The present paper gives evidence that films of pure alkaline earth oxide from one to 25 molecular layers thick deposited by evaporation can lower the thermionic work function of clean receiver metals by as much as 3.5 volts. The results are compared with published data on oxide-coated cathodes.

EXPERIMENTAL

Tube Construction

Consistent results were obtained in a variety of tube structures which evolved into two designs, one used only for thermionic tests and the other for both thermionic and contact potential measurements. The essential features of the thermionic tube are shown in Fig. 1. Five filaments, F_0–F_4, were mounted inside the anode system, F_0 along the tube axis and the others parallel to it at intervals of 90° around the circumference of a circle of 0.75-in. radius. When the relative effects of two oxides on a given receiver surface were to be compared, the central filament acted as the receiver and was a ribbon with its plane at an angle of 45° to the planes of the outer filaments, as shown. Repeated runs could be made by cleaning the receiver by flashing. The outer filaments served as sources from which oxides evaporated onto the receiver, for example, BaO from F_1–F_3, SrO from F_2–F_4. When effects of equal quantities of a given oxide on four different receiver metals were to be investigated, the central filament served as a source from which the oxide was evaporated, the four outer filaments F_1–F_4 acting as receivers. In such experiments, the cross section of the central source filament was circular. The filaments were $6\frac{1}{4}$ in. long. They were supported by springs S from a system of mica insulators M. To minimize end cooling effects, the anode system was divided into three sections D, A, and D, the central 1.5-in. section A collecting the emission of the central section of the receiver filament, with D and D serving as guard rings. All three sections of the anode were usually operated 135 volts positive with respect to the filament on test, the small correction for Schottky effect being of the same order as that for clean tungsten. The baffles BB_1 mounted between the outer filaments prevent material evaporated from any side filament from depositing on those adjacent, the section B_1 protecting the sections between the anode and guards. The filaments used as sources of the alkaline earth oxide consisted of a support (or core) of chemically pure platinum coated with about 5 mg per cm^2 of an alkaline earth carbonate of high purity. The carbonate was converted to the oxide during exhaust. A sample analysis of $SrCO_3$ is given:

Spectrochemical qualitative		Estimated range (percent)
Major component	Sr	
Trace	Ba, Mg, Ca, Na	<0.03
Slight trace	Bi, Fe	<0.005
Very slight trace	Ag, Al, Co, Mn, Si	<0.001

Spectrochemical quantitative	Weight (percent)
Ba	0.023
Na	0.016
Ca	0.041
Mg	0.009

In the contact potential tube the same guard ring structure was used. A section is shown in Fig. 2. Filaments 1 and 3 were receivers while 2 and 4 were sources, respectively, of Sr metal and of SrO. The strontium metal sources resemble commercial oxide-coated filaments except that the coat was pure SrO

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[1] Davisson and Pidgeon, Phys. Rev. **15**, 553 (1920).
[2] A. W. Hull, Phys. Rev. **56**, 86 (1939).
[3] A. W. Hull, U. S. Patent 2,246,176.
[4] Moore, Allison, and Morrison, Phys. Rev. **75**, 347 (1949).

and the support metal Konal or nickel containing approximately 0.1 percent by weight Mg. These are known[5, 6] to reduce alkaline earth oxides to free metals. Tests which will be described elsewhere indicate that at least 100 atoms of strontium metal evaporated for each SrO molecule. The central filament 5 was a source of electrons for the contact potential tests and was usually clean tungsten operated at about 1800°K, although oxide-coated filaments were used in some tubes. Because of shields *SS*, material evaporated from one source could not strike either filament 5 or the other source. Filament 5 was heated by a biased half-wave rectifier so that electrons could leave[7] only during the non-heating half-cycle.

Chemical Preparation and Exhaust

All platinum filaments, either oxide sources or receivers, were treated at 1000°C for 30 min. in hydrogen saturated with water vapor to oxidize[8] any impurity present in the platinum which might otherwise form free alkaline earth metal by chemical reaction with the oxide coat. The platinum was prepared by Mr. H. T. Reeve and was unusually pure, the only impurity spectroscopically detectable being copper present to less than 0.03 percent.

During exhaust, the 702-EJ glass was baked for several hours at 470°C or above, the molybdenum or tantalum anode sections were heated inductively and all source filaments were thoroughly heated. This process was repeated several times throughout a two- or three-day exhaust period. The receiver filaments were then flashed, the barium-magnesium getters *G* were vaporized and the tube sealed off.

The stability of the work function of a receiver throughout long periods of idleness indicated that the pressure of thermionically important gases in the volume of the tubes was very low. Thus a contact potential test of a clean tungsten receiver in any tube tested could be repeated to within 0.02 volt after an idle period of more than a month. This fact, together with relations found by Langmuir[9] for the adsorption of gases on clean tungsten, indicates that no gas or gases in the volume of the tubes capable of affecting the work function by 0.1 volt or more were present to as much as 10^{-14} mm. This high vacuum is believed dependent on a severe exhaust schedule, the gettering action of zirconium applied to the outer anode surfaces and to the BaMg getters, *G*. The writers acknowledge the skill with which Mr. E. A. Thurber supervised the application of zirconium and several other features in the chemical preparation of these tubes.

Temperature Determination

Temperatures of source and receiver filaments were measured pyrometrically, correcting for emissivity and transmission of the glass. When possible, resistivity relations were used in combination with the Stefan-Boltzman law to extend the temperatures to values

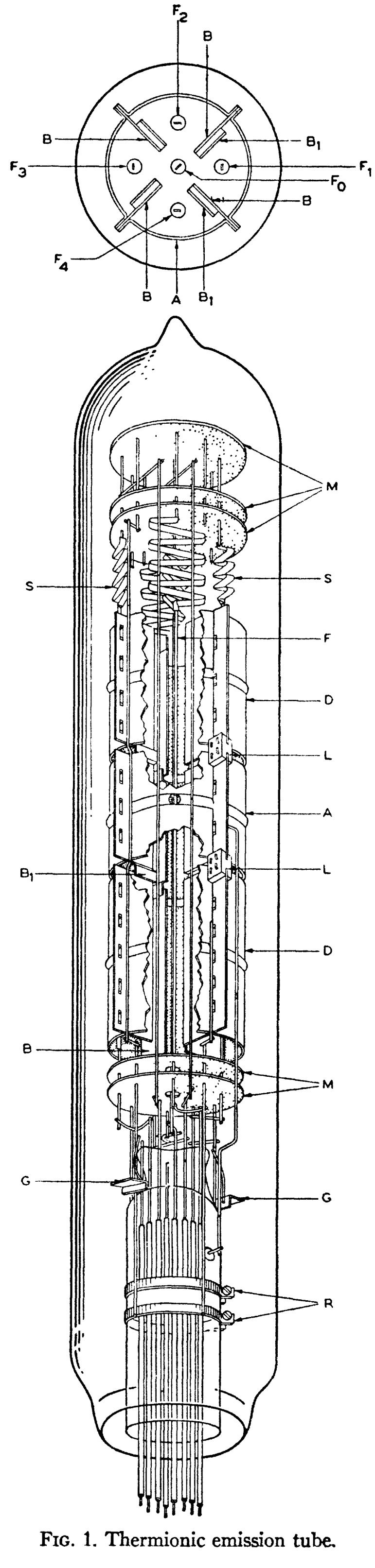

FIG. 1. Thermionic emission tube.

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[5] E. F. Lowry, Phys. Rev. **35**, 1367 (1930).
[6] M. Benjamin, Phil. Mag. **20**, 1 (1935).
[7] L. H. Germer, Phys. Rev. **25**, 795 (1925).
[8] C. H. Prescott, Jr., J. Am. Chem. Soc. **60**, 3047 (1938).
[9] I. Langmuir, Chem. Rev. **13**, 167 (1933).

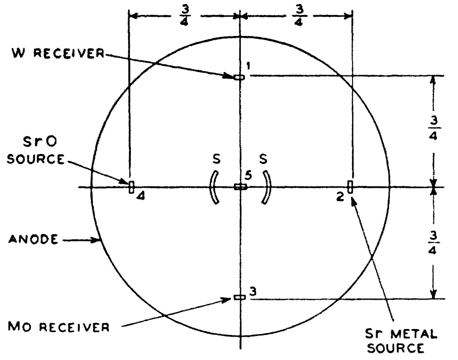

Fig. 2. Contact potential tube. (Filament 5 is electron source. S—S are shields to prevent evaporated material from striking filament 5.)

inaccessible by optical pyrometers. A curve of corrected temperature as a function of filament current for a typical molybdenum filament is given in Fig. 3 and similar curves were obtained for tungsten. The data from two different optical pyrometers, from resistivity, and from power radiated, are in substantial agreement. The spectral emissivities of the coated filaments were measured by reflectometer methods. It is believed that the probable absolute error in any temperature given is not over 10°C and the probable relative error between any two observations of the same filament is not over 5°C. The precision of temperature determination limits the precision with which Richardson constants can be stated. With the present techniques, thermionic measurements of coated tungsten or molybdenum receivers can be made over a range of about 150°C; interelectrode conductance prevented measurement of emissions less than about 10^{-9} amp. It was assumed that the temperature scales determined for the clean receivers were unchanged for coverings up to about 50 layers. This assumption is difficult to justify experimentally but electromagnetic theory indicates that the effect on emissivity should be negligible for less than about 200 layers.

Thermionic Measurements

A modification of the method described by Becker[10] was used to express many of the activation measurements. The receiver filaments were first cleaned by heating for 10 sec. to approximately 2800°K for tungsten or 2300°K for molybdenum after which the observed thermionic emission was that appropriate for clean tungsten or molybdenum. The source filament F_0 was then operated for approximately an hour at a known temperature and allowed to cool. Each receiver filament in turn was then heated at gradually increasing

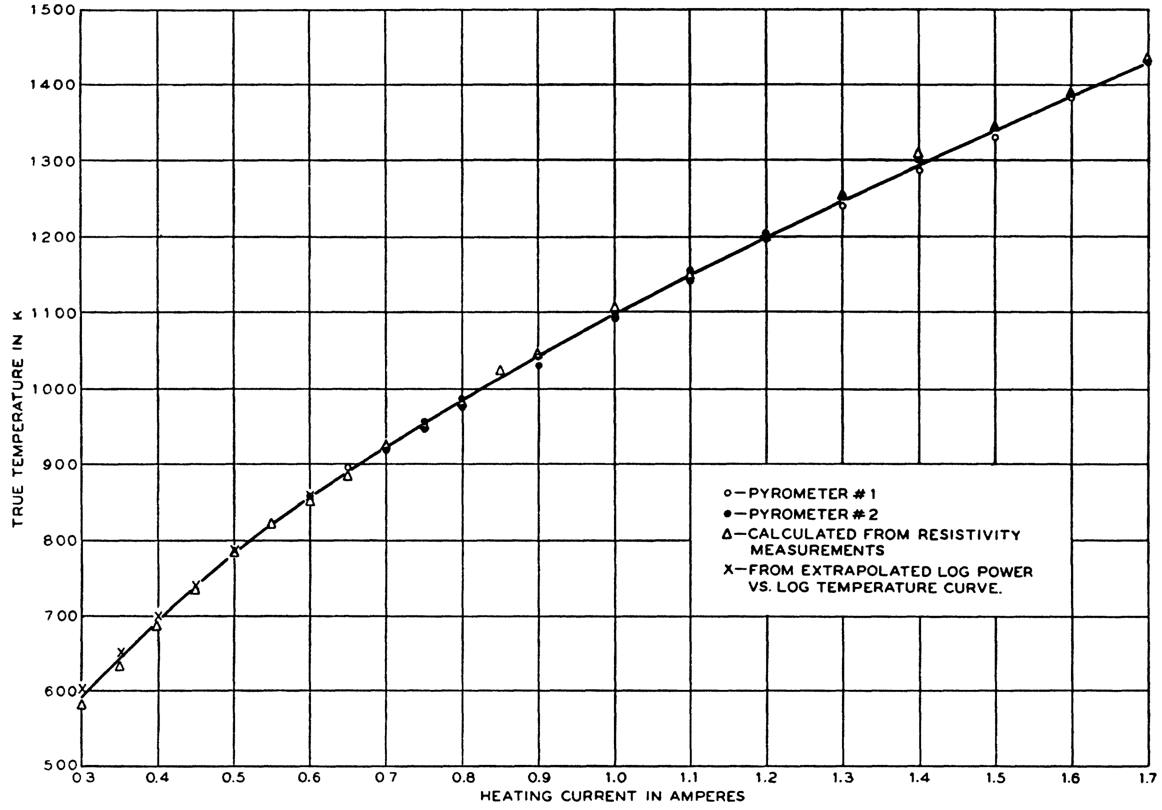

Fig. 3. Temperature-current characteristic for molybdenum receiver filament.

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[10] J. A. Becker, Phys. Rev. 34, 1323 (1929).

temperatures until its emission reached a reference value (usually about 10^{-8} amp./cm^2). The receiver temperature required for this emission was recorded and the receiver then allowed to cool. The sources were again heated for approximately an hour and the receiver retested. The receivers were thus activated by successive deposits and the temperature required for reference emission was then plotted against the time for which the source filament had been operated. Several such runs were made with each experimental tube, the receiver filaments being cleaned by flashing before each run. This is a convenient method for representing the enormous range of activation observed in a single coating run.

In many runs, emissions were measured over a range of temperatures after each increment of deposit. The data were usually expressible in terms of Richardson's equation* $I=AT^2\exp(-\varphi e/kT)$, φ and A being determined with precisions of about five percent and 50 percent, respectively.

Determination of Amount of Oxide Deposited

The amount of oxide deposited on a receiver was determined by two methods, neither depending on assumptions regarding observed thermionic effects. The amount vaporized from the source can be computed from the vapor pressure-temperature curve of the oxide. Then from tube geometry and the assumption that no molecules are reflected from the receiver, the amount intercepted becomes known. This method is not very precise, the probable error of 10° in the determination of source temperature being equivalent to about 50 percent error in amount evaporated.

The amount present on a receiver ribbon can be determined with a precision of one or two percent by using radioactive tracers in coating the source filament. After deposit and thermionic test, the receivers are removed from the tube and their count compared with that of an aliquot of the mixture used to coat the source. The methods agree well within the 50 percent uncertainty of vapor pressure determinations indicating that not over 50 percent of the molecules are reflected from the receivers.

Many of the results are expressed in terms of molecular layers computed by assuming that the molecules are adsorbed with the line of centers perpendicular to the receiver surface, each molecule occupying a circle of radius r_0 as defined by Slater.[11] This configuration is assumed primarily for convenience rather than because of a strong belief in its correctness.

RESULTS

Activation as Shown by Richardson Lines

Ideally one would hope to find a continuous curve, reproducible from tube to tube, showing the behavior of the Richardson constants A and φ as a function of the amount of adsorbed oxide for each combination of oxide and receiver metal. This ideal was but imperfectly realized.

The activation of four receiver filaments in tube No. 5 by depositing BaO is shown in Figs. 4 and 5, the first giving φ and the second $\log_{10}A$ as a function of the amount of BaO deposited, determined by the vapor pressure-temperature method. φ decreases very rapidly for the first 0.1 layer and then only very gradually to about 24 layers—the maximum covering applied in this run. For tungsten, molybdenum, and tantalum, φ drops to 1.0 volt or less, but for zirconium, the lowest work function realized was about 1.5 volts. The behavior of A is less easily described. Perhaps the only safe generalization is that A for the coated receivers is usually at least one order of magnitude less than for the clean receiver metals.

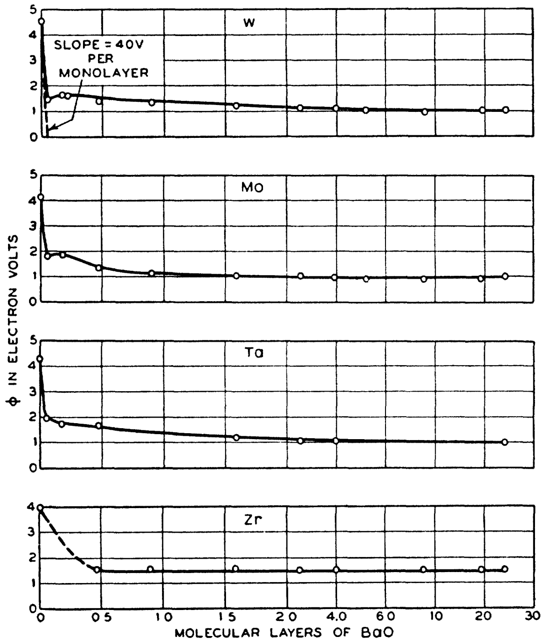

FIG. 4. Work function, φ, of receivers as a function of amount of BaO. Note change of scale in abscissas at 2.0 layers and at 6.0 layers.

More than 200 similar activation curves were taken. For successive runs on any particular receiver filament in a given tube, the emission current for a given amount of oxide and test temperature was reproducible to within less than ±50 percent for coverings of less than a monolayer, but became less reproducible for heavier coverings. In repeated runs on the same filament, the work functions usually agreed to within 0.1 volt but the reproducibility of A was poor. However, the experimental difficulty in obtaining reliable values for A, even for clean metals, is well known.

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* Values of φ taken from Richardson lines have been designated as φ^* by Herring and Nichols, reference 15.

[11] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), p. 381.

Activation by Modified Becker Method —Radioactive Tracers

Figure 6 shows a correlation between activation and amount of SrO evaporated onto three of the four tungsten receiver ribbons spaced around a SrO-coated platinum source filament. The amounts were determined with a precision of about two percent by tracers of radioactive fission strontium. The following results were obtained:

(1) During seven successive deposit runs, the emission *vs.* time of deposit data were reproducible for any one receiver but the time rates of activation differed by as much as a factor of two between individual receivers.

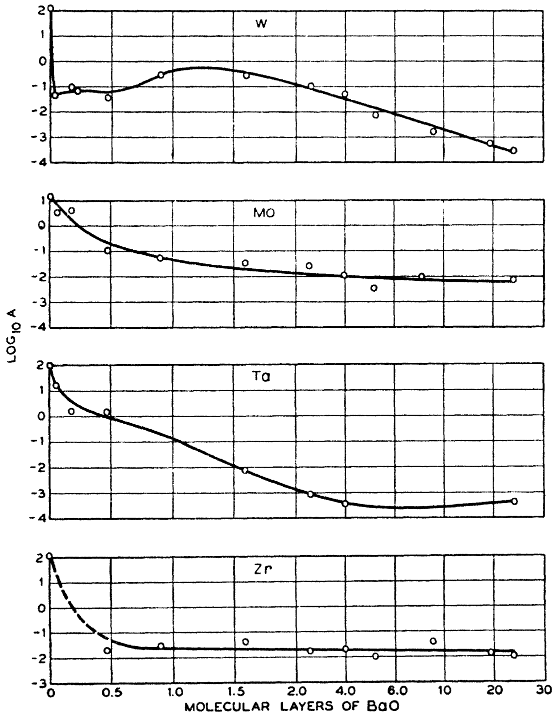

FIG. 5. Log_{10} Richardson A for receivers as a function of amount of BaO. Note change of scale in abscissas at 2.0 layers and at 6.0 layers.

(2) Assuming a uniform rate of deposit, the amount of SrO required for any particular activation was determined directly by removing the receiver ribbons at the end of the seventh deposit run and comparing the radioactive count from each receiver with that from an aliquot of the mixture used to coat the source. That this resolved the discrepancy in time rates noted in (1) is indicated by the agreement of data for the three receivers shown in Fig. 6. Note that each gave an emission of 6.7×10^{-8} amp. cm^{-2} at 650°±10°K for films from 0.3 to 1.0 $\mu\text{g cm}^{-2}$. In other tubes these same amounts of SrO often gave higher activation, the same emission requiring a temperature of 600°K or less. Heavier coverings, when accompanied by a treatment which consisted of heating the receiver for 2′ or 3′ at 900°K with or without space current, gave still higher activation (see Fig. 12, for example).

(3) Before opening the tube, the fourth tungsten receiver was heated at 1000°K for 60 hr. The resulting decay of emission was followed as a function of time; analysis then showed that the relationship of Fig. 6 held only for deposit. For simplicity in presentation, such decay phenomena will not be discussed further.[12]

Richardson Lines—Details

A few of the Richardson lines for one run in which a tantalum filament was exposed to BaO are shown in Fig. 7. One observes from the tabulated values in the figure that the work function and A both change during the run but not in a simple way. Occasionally, as the thickness of the deposited films increased and the filaments became more active, the Richardson lines were curved. In such cases, the curve was reproducible and always concave downward which is opposite to that expected for patch effects. The curvature is not caused by anode voltage effects, nor by inaccuracy in either temperature or current measurement. In all tubes studied, straight Richardson lines were obtained most consistently for films when the receivers were tantalum.

In Table I representative work functions and emissions are reported, together with values for oxide cathodes of the commercial type and various other emitters described in the literature. The first figure given for φ or emission for any thin film system applies to a monolayer while the second is for 10 to 30 molecular layers.

The data for the first three entries in Part C taken from Blewett,[13] are very conservative. When BaO and SrO are used together, the d.c. emissions realized commercially for the past decade are of the order 1–10 amp. In the present thin film experiments, emissions above about 150 ma/cm^2 were not directly observed; values above this level were obtained by extrapolation. By measurements in the temperature range 550–800°K, emissions above 2 amp./cm^{-2} at 1000°K were occasionally indicated.

Two similarities in Parts A and C of Table I are evident. First, the emissions for a commercial type of oxide layer are about equal to those found in the present work for thin layers of the same oxide on either tungsten or molybdenum. Second, CaO gives the least emission and BaO gives the highest in both the thick layers and the thin films. A difference not so evident in Table I should be noted; the best commercial cathodes use nickel as a support metal, but, in the one experiment with a nickel receiver, the emissions were low.

Contact Potential Measurements

The data of Table I were all obtained by thermionic measurements. However, the thermionic technique does not distinguish between the activation caused by the oxide as deposited, and any effects resulting from the required heating (to approximately 1000°K). Heating might cause physical or chemical changes in the struc-

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[12] Some preliminary data on decay are given in Eisenstein's review. See *Advances in Electronics* (Academic Press, Inc., New York, 1949).

[13] J. P. Blewett, J. App. Phys. **10**, 668 (1939).

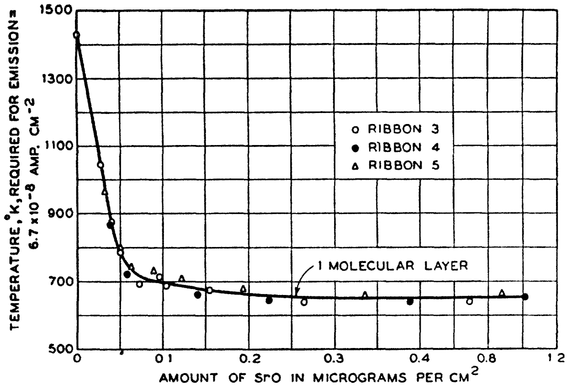

FIG. 6. Correlation between activation of tungsten and amount of SrO deposited.

TABLE I. Emission constants.

System	φ-volts	Temperature range of measurements —°K	Indicated emission at 1000°K —amp. cm^{-2}
Part A—Thin oxide films in present work (1–30 monolayers)			
BaO on Mo	1.2–1.0	550–900	0.6–1.0
SrO on Mo	1.2–1.1	550–900	0.6–0.8
CaO on Mo	2.1	820–920	10^{-5}
BaO on W	1.2–1.0	550–900	0.6–1.0
SrO on W	1.2–1.1	550–900	0.6–0.8
CaO on W	2.1	820–920	10^{-5}
BaO on Ta	1.3–1.0	600–900	10^{-3}–10^{-2}
SrO on Ta	1.3	600–870	10^{-3}
BaO on Zr	1.5	670–870	10^{-3}
SrO on Pt	1.9	600–960	10^{-5}
SrO on Ni	2.0	675–850	10^{-9}
Part B—Thin films described in literature			
Hull's dispenser[a]			
Cathode—BaO on Mo	1.215		0.63
Ba metal on W[b]	2.1		0.002
Ba metal on oxygen on W[c, d]	1.34		0.03
Part C—Thick oxide films of commercial type			
BaO[e]	1.1±0.3		10^{-3} to 10^{-1}
SrO[e]	1.4±0.3		10^{-4} to 10^{-2}
CaO[e]	1.9±0.3		10^{-5} to 10^{-3}
Commercial oxide cathodes 1936 to present			
Mixed BaO-SrO on Ni	1.2–1.0		1–10
Prescott's nickelated filament —best activity[f]	1.37		0.25

[a] See reference 2.
[b] J. A. Becker, Trans. Faraday Soc. **28**, 148 (1932).
[c] C. J. Smithells, *Tungsten* (D. Van Nostrand, Company, Inc., New York, 1936).
[d] A. L. Reimann, *Thermionic Emission* (John Wiley and Sons, Inc., New York, 1934).
[e] See reference 13.
[f] See reference 8.

ture of the system, which in turn could be partially responsible for the activations observed. By using contact potential tests, the nature of the active receiver system can be more definitely inferred. Since the measurement to be described depends on the shift in voltage-current characteristic for electrons flowing *into* the receiver against retarding fields, the activated specimens need never be heated after beginning a run. The effect of the oxide *as deposited* is therefore directly observed, and effects caused by heating can subsequently be evaluated. Answers to the following questions were sought: (1) How much activation is caused by heating the system during thermionic measurement? (2) The emission of a given layer of oxide on platinum is generally less than for the same layer on tungsten, molybdenum, or tantalum and also generally decays more rapidly during thermionic measurement. Is the tabulated lower activity for platinum receivers the result of decay before the measurement is complete, or inherent in the nature of the platinum surface? (3) Is

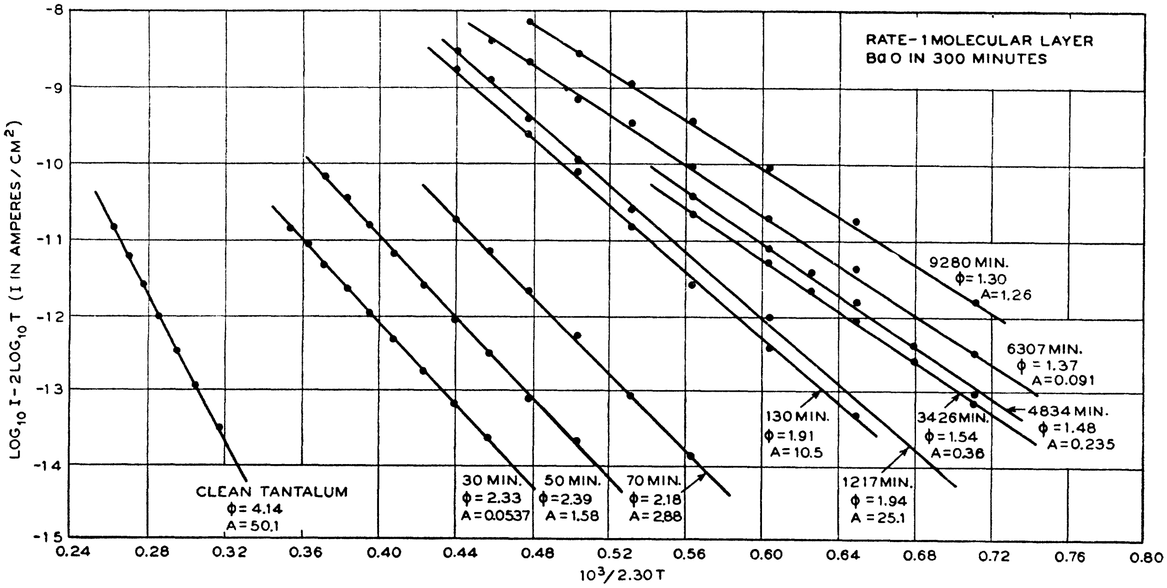

FIG. 7. Richardson lines for one run—BaO on tantalum. Each line represents a particular covering.

the deposited oxide in the form of agglomerates or a thin film?

These are taken up in turn:

(1) Four retarding field characteristics, corresponding to four different coverings (all less than monomolecular) of a molybdenum receiver during one coating run of SrO are shown on Fig. 8. The points for the curve farthest to the right represent clean molybdenum. The linear portion as drawn has a slope corresponding to an electron temperature[14] of 1826°K. The corrected pyrometer temperature of the electron source (a clean tungsten filament) was 1828°K. The difference between the two determinations is thus 2°K (less than the probable error of slope determination). When coating is applied to the receiver, the slope corresponds to a significantly higher electron temperature. The change of slope occurs even for the characteristic obtained after depositing oxide for 22.5 hr., corresponding to only 0.015 molecular layer. A line is then drawn through the lowest experimental point, parallel to the characteristic for the clean receiver.

Such changes of slope are probably a consequence of reflection caused by the known patch fields,[15] an effect which would prevent the method from indicating the full decrease in work function actually produced. Neglecting this effect, consider the characteristics for 133.3 and 317 hr. Until after the test corresponding to the deposit for 133.3 hr., the receiver was not tested thermionically and its temperature therefore was never more than a few degrees above ambient, so that the work function of the molybdenum had decreased by at least 1.20 volts as judged by the horizontal shift of the curve. It was then tested thermionically at a maximum temperature of 986°K for approximately 5 min. after which the contact potential test was repeated. The difference between the original contact potential test at 133.3 hr. shown by solid circles and the second test shown by small triangles indicated that φ increased by about 0.02 volt. A similar procedure was followed in the subsequent tests of this run. The thermionic tests never altered the work function of the receiver by more than 0.03 volt. At the 317-hr. test period shown, the thermionic test decreased φ, as measured by contact potential, by about 0.03 volt. These tests indicate that:

(a) Contact potential tests agree with Richardson plots in showing that thin films of the oxides activate the receivers and show, in addition, that the activation is caused almost entirely by the oxide *as deposited*, the heating during emission tests not being essential.

(b) For layers less than a monolayer, changes less than ±0.03

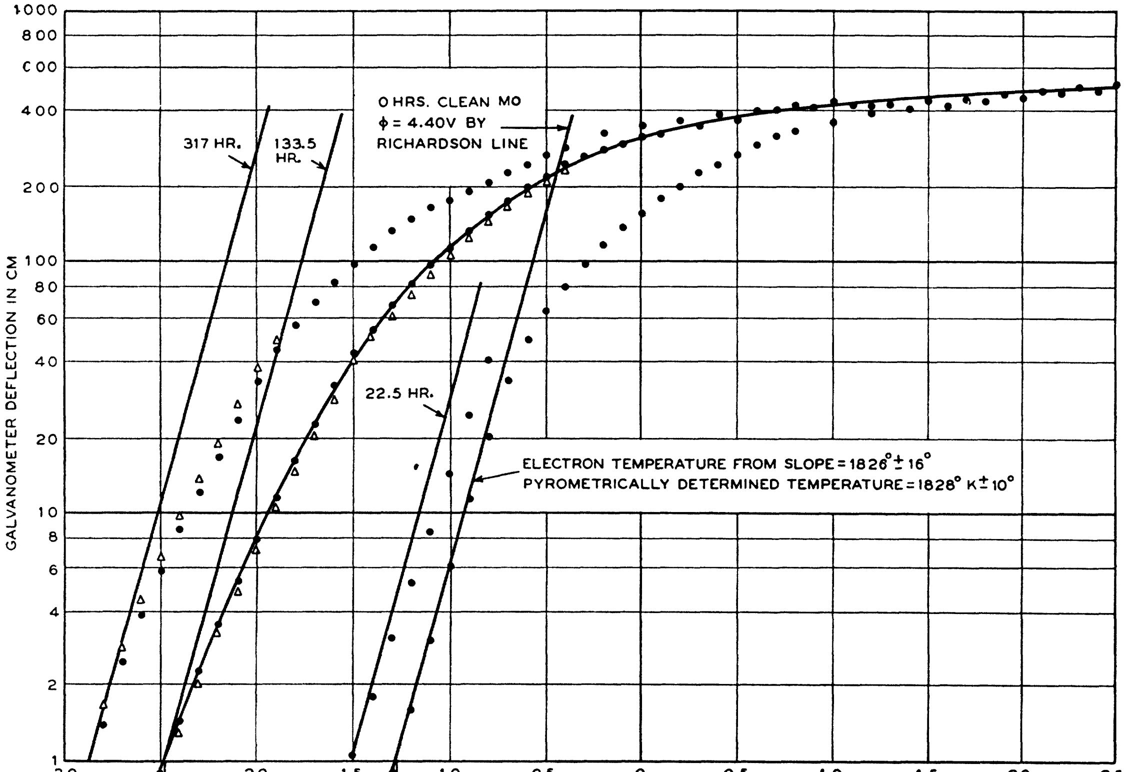

FIG. 8. Retarding potential lines as molybdenum receiver is coated with SrO.

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[14] See for example Millman and Seeley, *Electronics* (McGraw-Hill Book Company, Inc., New York, 1941), p. 161 ff.

[15] C. Herring and M. H. Nichols, Rev. Mod. Phys. 21, 185 (1949), see especially Fig. 18 and Chapter II.

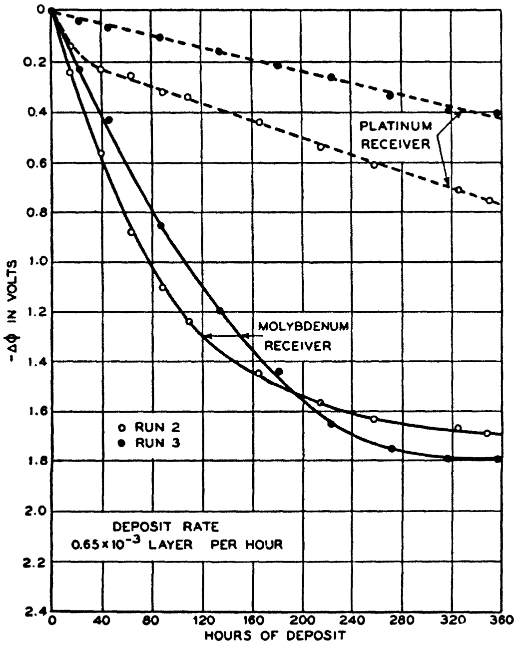

FIG. 9. Contact potential test—molybdenum and platinum receivers coated with SrO.

volt do occur as a result of incidental heating in thermionic tests. The corresponding change in the thermionic emission measured at low temperature is not more than a factor of three. For layers thicker than a monolayer, the activation by heating was often much greater than a factor of three.

Appreciable chemical reduction of adsorbed oxide to free strontium or barium is conceivable during thermionic tests. Contact potential tests, however, throw no light on this question because other experiments show that the change of work function is negligible when appreciable quantities of free strontium metal are deposited with the oxide. On this question one can therefore only conclude that if such reduction occurs, its effects are negligible for either contact potential or thermionic measurements of activation by monlayer films.

(2) Platinum activation was also studied in three tubes by contact potential tests in order to avoid heating the receiver during measurement. Contact potential curves, shown in Fig. 9, are derived from retarding potential curves such as Fig. 8 by plotting the shift of the retarding field characteristic against the amount of SrO deposited. Curves for platinum and molybdenum receivers on which the same amounts of SrO are deposited from the same source are shown in Fig. 9. No thermionic tests of the platinum were made during these runs except for the initial point, in which an attempt was made to obtain "clean" platinum. For run No. 2 the platinum was flashed for 10 sec. at $T=1800°\text{K}$ and the subsequent deposit of 0.23 molecular layer of SrO is seen to have decreased the work function by 0.775 volt. For run No. 3, the platinum was flashed 10 sec. at $T=1920°\text{K}$ and the deposit of the same amount of SrO decreased the work function by only 0.4 volt. Thermionic tests indicated that the platinum was considerably cleaner at the beginning of run No. 3 than for run No. 2. The contact potential tests thus indicate† that a given amount of SrO up to about 0.23 layer decreased the work function of platinum by much less than that of molybdenum.

(3) In contrast to Davisson and Pidgeon,[1] who concluded that the BaO on their receivers agglomerated, the deposit is here believed to form a thin film spread fairly uniformly over the receiver surface. This belief is based on the fact that the work function of a patchy surface as measured by contact potential is an arithmetical average of all patches, each weighted according to its area (reference 15, Eq. (II-4.3)). Thus, suppose that the deposited oxide became agglomerated into patches occupying about 10 percent of the area while the remaining 90 percent became uncoated. The work function of any patch must be positive so that the assumed agglomeration would give a contact potential only about 0.4 volt different from clean molybdenum. Such agglomeration is therefore inconsistent with the observed contact potential shift of 1.8 volts for 0.23 layer. The shift caused by a complete layer, if measured by a method not affected by reflection, would probably be considerably greater than 1.8 volts.

PURITY OF SYSTEMS

This work was intended as an examination of idealized thermionic systems, each containing in principle only a clean receiver metal adsorbing known amounts of pure alkaline earth oxide. The performance of these quantitatively specifiable systems was compared with that of the practical oxide cathode. The value of the comparison will depend on the degree to which the ideal system was experimentally realized.

Cleanliness of Receiver Metal Surfaces before Coating

If cleanliness is judged by agreement of observed thermionic data with generally accepted values in the literature, only tungsten, molybdenum, and tantalum receivers were made clean in these tubes. Filaments of less refractory metals, such as nickel, zirconium, or platinum, in general, could not be made clean at temperatures below melting, although many atomic layers of the support metal were vaporized from their surfaces. Because the emission from "soft" receivers in the cleanest condition attainable was always greater than the published values, it is believed that the residual higher activity is caused by alkaline earth oxide (deposited as a result of operating the source filament

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† The work function of the "clean" platinum as measured by Richardson plots was about 2.7 volts, but as measured by contact potential, the work function of the molybdenum and platinum were nearly equal at the beginning of the run. This indicates patches of about 2.7 volts work function over a small part of the surface of this "clean" platinum.

during exhaust or subsequently) that remains in or on these receiver metals until fusion.

Of the three refractory metals, which could be thoroughly cleaned by flashing, tungsten and molybdenum activated to approximately the same extent for a given deposit of BaO or SrO and tantalum activated somewhat less. In general, the emission of coated platinum or nickel receivers was considerably less but lacked the stability required for reproducible Richardson plots.

However, in one test, a Richardson plot for clean platinum was obtained having a work function $\varphi=4.43$ ev and $A=25$. This was one of the closest approximations in the present experiments to the "clean" value of 5.3 volts quoted[16] in the literature. After depositing one monolayer of SrO, a Richardson plot at temperatures between 860°K and 960°K indicated a work function $\varphi=1.9$ ev and $A=0.01$. Measurement above 960°K caused deactivation. This was also one of the highest and most stable activities attained with a platinum receiver and was used for the platinum entry of Table I.

Only one nickel receiver was examined. It was flashed at higher and higher temperatures prior to each successive deposit run. Although this flashing increased the activation obtainable from a given deposit of SrO, the highest emission observed prior to burning out the nickel was that indicated in Table I. The nickel when last flashed was probably much cleaner than that in commercial cathodes.

In summary, the tungsten, molybdenum, and tantalum receivers are believed to have been clean before coating, the other receivers were not. Additional attempts will be made to prepare clean platinum receivers before coating.

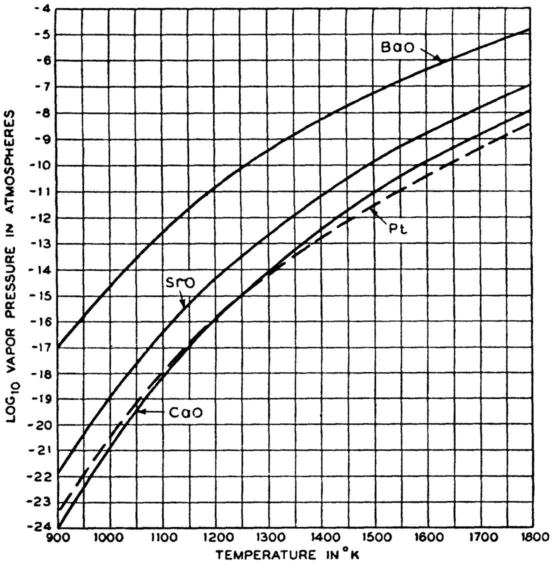

FIG. 10. Vapor pressure of alkaline earth oxides and of platinum.

Purity of Evaporated Product

The purity of the product evaporated from the source filaments is of paramount importance and was examined in four respects, listed (A), (B), (C), and (D).

(A) Is free calcium, strontium, or barium metal evaporated with the corresponding oxide? Three types of evidence combine to indicate that very little free metal is evaporated, and that any probable amount would have no appreciable effect on these thin film systems.

(a) Attempts were made to determine experimentally the amount of free metal evaporating with the oxide. Wooten's hydrogen evolution technique[17] was applied to special tubes containing only the pure platinum filament, treated in wet hydrogen and coated with the same pure alkaline earth carbonates as in the thermionic and contact potential tubes. Because of the present sensitivity limit of the method (about 1 μg), the results merely placed an upper limit of about 0.1 percent on the ratio of free metal to oxide evaporated. This ratio is sufficiently small to justify the working assumption, always tacitly made in measuring the vapor pressure, that the reduction of alkaline earth oxide either by heat alone or by contact with hot platinum is negligible. However, this experimental result in itself, is not sufficient to exclude the possible deposit of minute amounts of free metal which might be significant for semiconductor effects.

(b) A number of tubes were made in which the alkaline earth oxide was evaporated from a very pure Al_2O_3 ceramic source, with the thought that chemical reduction by such a ceramic would be even less probable than by platinum. Receivers were activated equally well by material evaporated either from the ceramic or from the platinum.

(c) Although the results will not now be given in detail, activation by evaporated free alkaline earth metal was compared with activation by evaporated oxides in several tubes of the contact potential design. It was shown that the deposit of appreciable quantities of free metal on a receiver already coated with the corresponding oxide caused very little or no additional activation. This same result occurred if the free metal were deposited at any time during the deposit of oxide and indicates that any free metal inadvertently evaporated from the oxide sources has no important effect.

(B) How much platinum evaporates with the oxide? Comparative vapor pressure curves, given in Fig. 10, were plotted from the measurements on the oxides by Claassen and Veenemans,[18] Blewett, Liebhafsky, and Hennelly,[19] and results from these Laboratories; the data of Jones, Langmuir, and Mackay[20] were used for platinum. The figure indicates that about one platinum atom evaporates for every CaO molecule, one for every 30 SrO molecules, and one for every 10^5 BaO molecules. Experience indicates that the rate of evaporation of support metals through these thick oxide layers may be about 30 percent as great as from the uncoated support metal. Accordingly, an appreciable amount of platinum

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[16] L. V. Whitney, Phys. Rev. 50, 1154 (1936).

[17] This method was discussed orally by L. A. Wooten, Phys. Rev. 69, 248 (1946), but has never been adequately published. However, it has given good results in many tests over a 15-yr. period in these Laboratories; see, for example, G. E. Moore, J. Chem. Phys. 9, 427 (1941).

[18] Claassen and Veenemans, Zeits. f. Physik 80, 342 (1933).

[19] Blewett, Liebhafsky, and Hennelly, J. Chem. Phys. 1, 478 (1939).

[20] Jones, Langmuir, and Mackay, Phys. Rev. 30, 201 (1927).

is probably present in the evaporated deposits, especially from calcium oxide sources. Because Becker and Sears[21] showed that evaporated platinum deactivates tungsten, the observed activations are at present thought to be less than would have been observed in the absence of this platinum. Only for BaO is this deactivating effect believed negligible.

(C) How much electronegative gas is evaporated together with the oxide? The authors of all published thermionic measurements on clean platinum emphasize the difficulty in eliminating oxygen and other electronegative gases. All such authors treated their filaments far more severely than is practical for the coated sources of the present work. It is therefore believed that a small but undetermined fraction of the evaporated product is electronegative gas and because these are known to deactivate tungsten and molybdenum, the activations given above are believed less than would be expected in the absence of such gas. CO_2 from carbonates undissociated in exhaust would also cause deactivation.

(D) What other impurities evaporate with the oxides? The only important spectroscopically detectable impurities found present in any oxide is one or more of the other oxides. BaO, to the extent of even a fraction of one percent in either SrO or CaO, can introduce serious errors of interpretation because its vapor pressure is orders of magnitude higher than that of either SrO or CaO, and because BaO apparently vaporizes from such mixtures much more rapidly than predicted from Raoult's law. These effects are illustrated in Fig. 11 for a SrO source contaminated with 0.47 mole percent of BaO. The abscissas were calculated from the vapor pressure of SrO and the corrected temperature of the source filament, assuming that only SrO was evaporated. The curve marked "0 hours" suggests that tungsten could be fully activated by about 0.001 monolayer of SrO. Many such curves were obtained with different tubes and this result was originally so interpreted.[22] However, after heating the source filament for long periods at 1460°K, cleaning the receiver filaments, and repeating the experiments, curves such as those designated "100 hr." and "1540 hr." were obtained. Because of preferential evaporation of BaO, the SrO source was gradually purified until after 1540 hr. at 1460°K it was essentially free of BaO. That this source of error has been eliminated from the experiments discussed above is illustrated in Fig. 12, giving results for a SrO source containing only 0.025 percent BaO instead of the 0.47 percent in the preceding figure. Data are plotted for three runs at ages 0, 101, and 775 hr. The points show that there was essentially no disagreement in the data for these runs.

For the above reasons the systems studied are believed good approximations to the ideal of a clean receiver metal on which known amounts of pure alkaline earth oxides are adsorbed. Any experimental deviations from this ideal are believed to decrease the activation, yet the observed thermionic emissions from these approximations to the ideal are comparable in magnitude to that of the commercial oxide cathode.

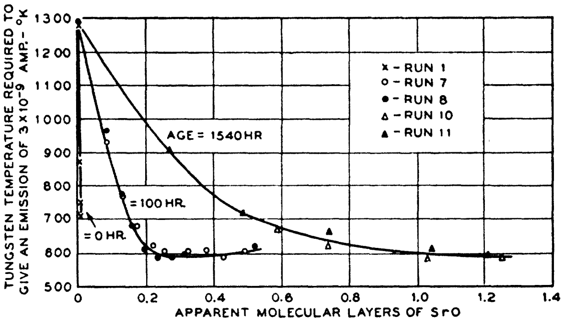

FIG. 11. Progressive purification of SrO source as indicated by time required for activation of tungsten ribbon. SrO contains 0.47 percent BaO.

DISCUSSION

The results may be explained tentatively by considering the alkaline earth oxide molecules to be strongly polar and preferentially adsorbed with the oxygen atom adjacent, and the line of centers perpendicular, to the receiver metal surface. Such an arrangement would appear probable if (1) other evidence indicates that the oxide molecules have a dipole moment with excess positive charge near the metal atom and (2) if the oxygen atom tends to be adsorbed preferentially toward the receiver surface.

Evidence for Polar Nature of Oxide Molecules

The three oxides in their crystalline state are usually considered ionic.[23] In contrast to DeBoer and Verwey,[24] the writers believe that the molecules are also ionic in the gaseous phase, and therefore probably in the adsorbed phase. The principal reason for disagreement with the above authors is their recognition of only two possibilities—that the molecule is formed either of doubly charged ions or of neutral atoms. The criteria for ionic nature given by Herzberg[25] were applied to the gaseous molecules considering the barium and oxygen as either doubly or singly charged ions. The results indicated that the gaseous molecule might not be doubly charged ionic but was almost surely singly charged ionic, and that the dipole strength was greatest for BaO and least for CaO. This same order also prevails in the dielectric constant[26] and in the tendency

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[21] Becker and Sears, Phys. Rev. 43, 1058 (1933).

[22] Oral reports before the American Physical Society, Phys. Rev. 69, 248 (1946).

[23] See for example, Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940).

[24] DeBoer and Verwey, Rec. Trav. Chim. Pays-Bas 55, 443 (1946).

[25] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 400 ff.

[26] K. Hojendahl, Kgl. Danske Vid. Sels. Math.-fys. Medd (1938).

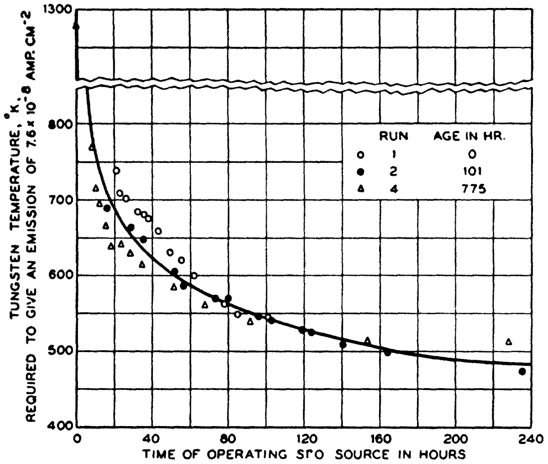

FIG. 12. Activation of tungsten receiver by SrO from source containing 0.025 percent BaO. Source temperature = 1470°K 0.058 molecular layers SrO deposited per hour.

of the oxide molecules to form compounds;[27] these differences could well account for the fact that BaO activates the receiver surfaces more than CaO. Furthermore, the differential rate of activation of a clean receiver (40 volts per monolayer in Fig. 4) is approximately that calculated if each adsorbed molecule lowers the work function by the amount expected from a singly charged ionic dipole in the most favorable orientation. The activation curves suggest that later arriving molecules are much less effective. It is therefore thought that the adsorbed molecules are strongly polar and as the distance between adjacent molecules decreases, there is a tendency for some of the molecules to reverse their orientation and form a "two-dimensional crystal."

Evidence That Oxygen Atom is Adjacent to Receiver Surface

One might infer that the oxygen would tend to be toward the receiver surface from the fact that Langmuir[9] has shown that only half of a monatomic film of oxygen atoms on tungsten will leave in 3 yr. at 1500°K while experiments by the writers suggest that nearly all Sr atoms will leave in 5 min. at this temperature.

Multilayer Films

The structure of the multilayer films is probably much more complex than for the monolayers; this would be expected from the strong affinity of one oxide molecule for another as indicated by the large heats of evaporation of the bulk oxides. However, one can infer that the semiconductor mechanism proposed for bulk oxide cathodes is probably not operative in even the thickest films examined in the present experiments. According to this theory,[13,28] the work function of the thick oxide layer in practical cathodes is determined essentially by the energy and concentration of impurity levels in the oxides. However, this does not seem probable‡ even in the thicker films of the present work. For example, 25 layers, shown in Fig. 4 to reduce the work function of tungsten from 4.5 volts to 1.0 volt, is about 10^{-6} cm thick, which is only a small fraction of the "exhaustion layer" within which the electrostatic potential in a semiconductor adjusts itself from the value at the plane of contact with the metal to the value characteristic of the bulk semiconductor. The change of potential V_D, in an exhaustion layer of thickness l and donor concentration n_D, is[29]

$$V_D = (2\pi e n_D l^2)/\epsilon,$$

where ϵ is the dielectric constant.[26] We take the values $\epsilon = 14.3$, $n_D = 10^{17}$, the upper limit for experiments on commercial-type coatings described by Wooten,[26,30] $l = 10^{-6}$ cm, for the thickness.

This gives 2×10^{-5} volt e.s.u. or 6×10^{-3} volt practical, an insignificant fraction of the change in work function which is produced by changes in activation of a thick coating. It seems safe to conclude therefore that the measured work functions shown in Fig. 4 are determined primarily by the nature of the double layers at the receiver-oxide and oxide-vacuum interfaces and have no particular relation to the existence of small amounts of volume impurities of the sort postulated in the semiconductor theory of the usual thick oxide coating.

Meaning of Thin Film Experiments for Practical Oxide Cathode

While the similarity in *magnitude* of emission is *not* intended as direct evidence for similarity in nature of the emission process in the two systems, the results are suggestive regarding one feature of current theories describing the oxide cathode as an electronic semiconductor in which excess barium (or strontium) metal governs both emission and conductivity. This emphasis on excess barium as an activating agent began with the papers of Koller[31] and Becker.[10] After about 1931,[13,32,33] emphasis shifted from barium on the outer surface of the oxide to barium in the lattice.

Turning to experimental evidence, one notes:

1. Results described above indicate that high thermionic emission is developed in thin oxide film systems containing essentially no excess alkaline earth metal either in the oxide layer or on its outer surface, and the addition of alkaline earth metal to these systems causes no appreciable increase of emission.
2. Widespread experience over the past 20 years has produced no satisfactory evidence that either the conductivity or emission

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[27] Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

[28] Hannay, McNair, and White, J. App. Phys. **20**, 669 (1949).

‡ The material in this section on multilayer films was largely suggested by Conyers Herring.

[29] W. Schottky, Zeits. f. Physik **118**, 539 (1942).

[30] See also Jenkins and Newton, Nature **163**, 572 (1949).

[31] L. R. Koller, Phys. Rev. **25**, 671 (1925).

[32] Becker and Sears, Phys. Rev. **38**, 2193 (1931).

[33] Fowler and Wilson, Proc. Roy. Soc. **137**, 503 (1932).

of thick oxide cathodes under practical operating conditions is related to excess barium, despite several attempts to produce such evidence. The most careful tests[17,30] show that if there is any correlation between barium content and emission, it can exist only for less than one atom of barium to 10^4 or 10^5 molecules of (BaSr)O.

3. Over the past 30 years, the emissions from thick layer, practical cathodes and from thin films of the type described above have both increased by a factor of more than 1000. For example, Arnold[34] stated that the commercial cathodes of 1920 emitted about 1 ma/cm^2 at 1000°K while today they emit at least 10^3 ma. Similarly, Davisson and Pidgeon[1] gave the emission of thin BaO films, prepared by methods nominally the same as those in the present experiments, as 0.3 ma at 1000°K; the films in the present work emit at least 10^3-fold more. This increase during the past 30 years in the emission of the thin film system cannot be related to barium metal and no published evidence justifies attributing the improvement in commercial cathodes to this cause.

While other analogous features of the two systems could be listed, a major point of dissimilarity should be emphasized. The evaporated deposits in the present work probably form true thin film systems, the adsorbed oxide acting entirely to lower the surface potential barrier for emission from clean receiver metals. In the practical oxide cathode, on the other hand, every experiment designed as a test indicates that the oxide layer is an electronic semiconductor; perhaps the most striking was performed by Hannay, McNair, and White,[28] who observed during activation the functional relationship between emission and conductivity implicit in the theory. One must conclude from their experiments that conductivity and emission of thick layers are governed by the same factors, although they do not necessarily support a mechanism based on excess barium.

If the thin film process is of importance in practical oxide cathodes the electrons could either be emitted at the interface, diffusing outward through pores without ever being incorporated into the lattice, or they could be conducted in the lattice to bits of support metal, or other substance which strongly adsorb the oxide, and then emitted by a thin film process from these particles which might be present in the outer layers of the oxide. The first mechanism would require a reflection coefficient of 0.9 or more for slow electrons striking oxide crystals. The work of Brown[35] suggests that such a reflection coefficient exists; however, this cannot yet be considered established. The great advantage of BaO, either pure or mixed with SrO, over either pure SrO or CaO as a coat for oxide cathodes is easily explained in terms of either mechanism as an equilibrium between molecules in the absorbed and crystalline phases; the relatively great energy binding the SrO or CaO molecules to their crystal lattice decreasing the fraction in the adsorbed phase. Further discussion of these speculations without additional evidence seems useless.

CONCLUSION

It has been established that the deposit of films in the range from one to 25 monolayers of BaO, SrO, or CaO on clean refractory metal surfaces reduces their thermionic work function, as measured by Richardson plots, by several electron volts. This effect can be qualitatively explained in terms of oriented dipoles.

Within the uncertainty of the experiment, the work functions obtained agree quantitatively with those published by others for bulk oxide coatings, which are ordinarily explained in terms of their properties as semiconductors. There is at present no theoretical reason for expecting such agreement. Further work is necessary before one can decide if the thin film mechanism is of any importance in practical cathodes, the present results being of the nature of necessary, but not sufficient, conditions for such importance.

The writers appreciate the help and advice of many colleagues, of whom only a few can be named. W. D. Stratton and H. W. Weinhart were responsible for mechanical design and construction. We acknowledge original ideas and other help resulting from discussions, especially with Conyers Herring, A. H. White, and J. A. Becker.

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

[35] B. B. Brown, thesis, M.I.T. (1942), not formally published.

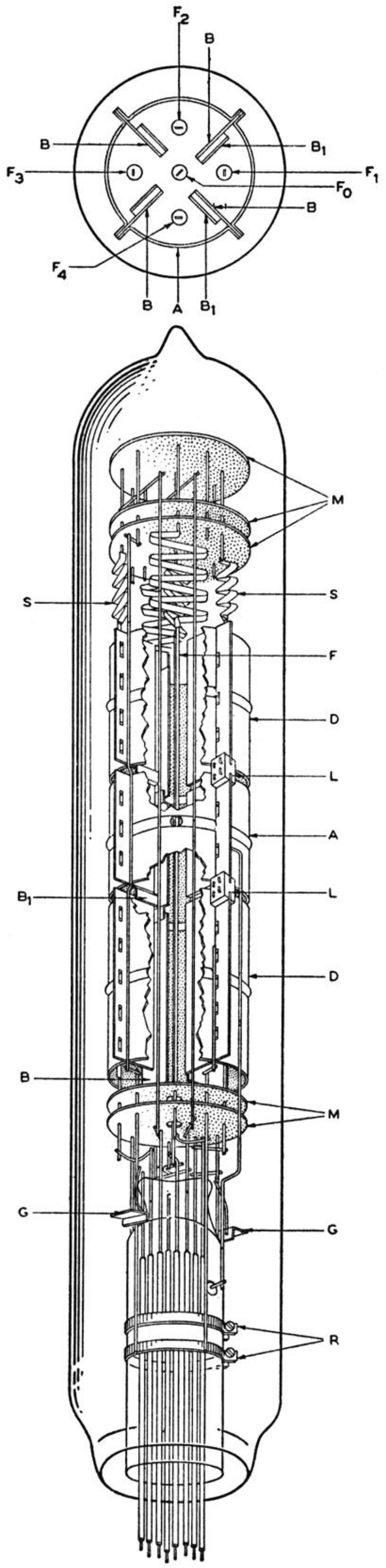

FIG. 1. Thermionic emission tube.