Thermionic and Adsorption Characteristics of Thorium on Tungsten

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Variation of thermionic emission of tungsten with surface density of adsorbed thorium.—Thorium was deposited on a tungsten ribbon by evaporation from a thorium wire. A study was made of the dependence of the thermionic emission on the two parameters: T, the temperature, and f, a quantity which is proportional to the amount of thorium on the tungsten surface. At a fixed temperature 1274°K it was found that as the amount of thorium on the tungsten surface was increased, the thermionic emission increased to a maximum, then decreased, and asymptotically approached a constant value. For the maximum, f is defined to be 1.0. The maximum value and the final constant value of the emission current were respectively 5.7×10^5 and 5.7×10^4 times the value of emission current characteristic of clean tungsten. Moreover the final constant value of the emission agreed to within a factor of 2 with the value characteristic of clean thorium. From $f=0.0$ to $f=0.8$ the relation between the emission current and f satisfied the following empirical equation

$$\log_{10} i = -3.14 - 6.54\ \epsilon^{-2.38f},$$

where i is the emission current in amperes per cm². For $0.8<f<2.0$, the values of emission currents are tabulated. For any fixed f, the emission obeys Richardson's equation. All the Richardson lines for $0<f<1$ intersect in a common point at an extrapolated temperature of 12,500°K, and for $f\geq1$ the lines intersect in a common point for which the temperature is 3250°K. These results obtained by depositing thorium on a tungsten ribbon have been compared with results obtained from thoriated tungsten wire. Thoriated tungsten wire can be activated by diffusion of thorium from the interior to the surface. For a while every atom that diffuses to the surface sticks to it so that f increases linearly with the time; later when evaporation is no longer negligible the rate of accumulation, df/dt, gets less and less; a steady state is reached when the diffusion rate equals the evaporation rate. It is unnecessary to assume "induced evaporation" to explain these results.

Variation of emission from thoriated tungsten with applied field.—It was found that for both the ribbon and the thoriated tungsten wire the dependence of emission on applied field changed as f was varied. For the thoriated tungsten wire the dependence of the thermionic constants A and b on applied field was most pronounced for $0.3<f<0.6$.

Evaporation and migration of thorium on tungsten surface.—Evaporation and migration of thorium on the tungsten surface were studied. The evaporation rate depends on the temperature and the fraction of the surface covered (f). For $0.2<f<1.0$ the rate of evaporation is approximately an exponential function of f. At 2200°K and $f=0.2$ the rate of evaporation was 10^{-4} layers/sec. and at $f=0.8$ was 31×10^{-4} layers/sec. It was found that thorium could be deposited on one side of the tungsten ribbon and then made to migrate to the other side of the ribbon. This migration occurred at an appreciable rate above 1500°K and was not complicated by evaporation up to 1655°K. It was found that the migration coefficient depended on f as well as on T. For a given set of conditions an approximate value of the heat of migration was calculated to be 110,000 calories per mol.

INTRODUCTION

THE saturated electron emission per unit area from a clean tungsten surface is a function of two variables, the absolute temperature and the applied field tending to pull the electrons away from the tungsten. When the tungsten surface is covered with one or two layers of foreign material the electron emission depends also on the amount and nature of foreign material. Thorium on tungsten is an example of such a case.

Langmuir[1] investigated the electron emission from thoriated tungsten filaments. He determined the activity[2] as a function of the time of flashing the filament at some activating temperature between 1800°K and 2200°K. His results are expressed in terms of a parameter θ which he defined as the fraction of the surface covered with thorium. Actually, however, all of his numerical values of θ are based on a theoretical formula which states that the logarithm of the electron emission from the surface varies linearly with θ. Dushman and Ewald[3] made a determi-

[1] Langmuir, Phys. Rev. **4**, 544 (1914) and **22**, 357 (1923).

[2] Saturated electron emission current per sq. cm at a particular temperature.

[3] Dushman and Ewald, Phys. Rev. **29**, 857 (1927).

nation of log i as a function of the absolute temperature for various activities of the thoriated tungsten wire. In both cases the thorium was brought to the tungsten surface by diffusion from the interior.

A more direct method of studying this problem is to deposit thorium on a tungsten ribbon by evaporation from a filament of pure thorium. This method has two distinct advantages. The first is that the amount of thorium deposited on the side of the ribbon towards the thorium wire is proportional to the time of evaporation at a fixed temperature. The second is that the amount of thorium that can be deposited on the tungsten is not limited to about one layer. This method of deposition of thorium on tungsten has been used in this investigation.

Experimental Procedure

The procedure followed can be outlined in the following manner. The dependence of the activity on the amount of thorium on the tungsten surface was determined. This was done for a particular temperature of the surface and for a given applied field. Then the activity was determined as a function of the temperature for various amounts of thorium on the surface and for the same value of the applied field. This much was sufficient to determine the activity as a function of the two parameters, temperature and amount on the surface. The relation between the activity and the amount on the surface was then used to study changes in the amount of thorium on the tungsten ribbon caused by flashing the tungsten ribbon at given temperatures. This treatment can cause migration from one side of the tungsten ribbon to the other, diffusion into the tungsten or evaporation from the tungsten surface.

Three similar tubes were used in this work. The essential features of one of the tubes are shown in Fig. 1. A tungsten ribbon filament B was mounted in the axis of the tube. In the plane of the ribbon were two shields S. On both sides of this plane, sectored cylindrical collectors were placed. The side view indicates that each collector was divided into three sections, two end collectors and a central one. A thorium wire,[4] A, was mounted on one side of and parallel to the tungsten ribbon. On the other side a 4-mil thoriated tungsten wire, C, was mounted. Four auxiliary 4-mil thoriated tungsten filaments were mounted on the outside for outgassing and clean-up purposes. Except for the filaments, the platinum leads in the press and molybdenum

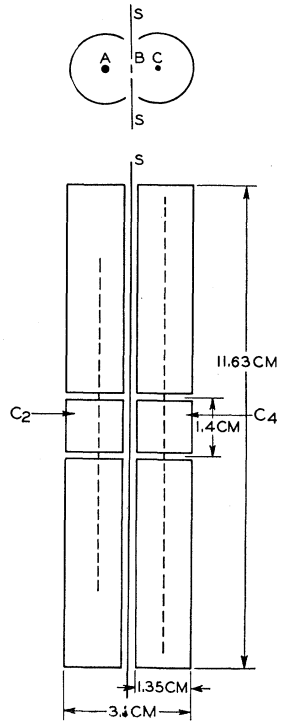

Fig. 1. Simplified diagram of filaments and plates. A, 0.038 cm, thorium wire, 7.9 cm long; B, 0.035 x 0.0036 x 11.1 cm, tungsten ribbon; C, 0.01 cm, thoriated tungsten wire; S, nickel shields; distance $AB=0.635$ cm.

springs to keep the filaments taut, the parts were constructed of preglowed nickel. An ionization manometer was sealed onto the side of the tube.

The design was based on the following considerations. A tungsten ribbon was used in order that the thorium could be deposited *uniformly* on a definite portion of the tungsten surface. It was essential to design the tube so that the electron emission from the two sides of the tungsten ribbon could be separated. This was the purpose of the shields. The central collectors C_2 and C_4 made it possible to measure the emission from a small central portion of the tungsten ribbon. This served two purposes. It reduced the effect of temperature variation along the ribbon

[4] We are indebted to the Westinghouse Lamp Company for this wire

due to end cooling and also reduced the effects due to non-uniform deposition of thorium along the length of the tungsten ribbon.

The emission from the tungsten ribbon was measured by maintaining the potential of all the plates positive with respect to the ribbon. Different applied potentials on the shields were tried. All of the readings used were taken with the shields at the same potential as the plates.

The temperature of the tungsten ribbon was determined as a function of the heating current by sighting on the ribbon with a Siemens and Halske optical pyrometer. Correction was made for the absorption of the glass wall of the tube. The true temperature was determined from the brightness temperature by using the known values[5] of spectral emissivity for tungsten. A temperature scale for the ribbon can also be determined from the tables given by Langmuir and Jones.[6] These two temperature scales agreed to within 10°, for the range 1200°K to 2000°K. Below 1200°K, Langmuir and Jones' table, because of end cooling, was not applicable.

Preliminary Treatment of Tubes

Each tube was thoroughly treated on the pumps for three days and sealed off at a pressure of 10^{-6} mm of mercury. During seal-off all the plates in the tube were kept hot (barely visible), by electron bombardment from the auxiliary filaments.

After a tube was sealed off, it was cleaned up by glowing the auxiliary filaments at 2500°K until the pressure was less than 10^{-8} mm of mercury. During this process a small current was drawn from these filaments to ionize the atoms of the residual gas. The other filaments were flashed from time to time to clean their surfaces and to condition them. The approximate value of the final pressure obtained was 5×10^{-9} mm of mercury. The final working condition of the tubes was such that any and all of the filaments could be moderately heated without affecting the pressure reading on the manometer. Severe heating of a filament, such as glowing the tungsten ribbon at 2800°K however, always caused a small temporary increase in pressure.

[5] Worthing and Forsythe, Astrophys. J. **61**, 146 (1925).
[6] Langmuir and Jones, Gen. Elec. Rev. **30**, 310 (1927).

At first the surface of the thorium wire was not clean and consequently the material evaporating from it was not pure thorium. Hence it was necessary to clean the surface of the thorium filament during the clean-up process. This could not be accomplished on the pumps because, at pressures from 10^{-7} to 10^{-6} mm of mercury, glowing the thorium filament caused it to take up gas. It was only at pressures of 10^{-7} or better that this effect ceased to be appreciable. The thorium wire could not be cleaned quickly because parts of it became clean before the rest. The clean parts had a lower emissivity than the others and consequently a higher temperature and a faster rate of evaporation. If therefore, the filament was run at too high an average temperature the increased evaporation from the clean parts reduced the size of the filament in spots. This effect would have rendered the filament useless. It was found that the filament could be got to a uniformly clean state by heating it at a low enough temperature for a long enough time (1000 hr. or more).

The effect of the material which evaporated from the thorium wire on the activity of the side of the tungsten ribbon towards the wire was studied. This was accomplished in the following manner. The tungsten was first flashed at 2800°K to clean it. Then the thorium wire was glowed for definite successive intervals. After each interval the activity of the tungsten ribbon was measured at some low testing temperature.

It was found that the results of successive tests of this kind changed continuously as the thorium wire was being cleaned off. At first, the deposited material decreased the activity of the tungsten; later it increased the activity up to some limiting value. Still later, a stage was reached where the deposited material first increased the activity to some peak value, and then decreased it.

At this stage another type of test was made. After a certain amount of material had been deposited on the tungsten, it was then removed slowly by glowing the tungsten ribbon at moderately high temperatures. The changes in activity during this removal process were followed. It was found that if the deposition had been carried to a stage where the activity passed through a peak, the activity on removal went back through a peak. Furthermore, the heights

of the peaks on successive removal tests were always approximately the same. At first the height of the peak on deposition was somewhat less than the height on removal. For each successive test the peak on deposition increased until finally it was somewhat higher than the peak on removal. As the treatment of the thorium wire progressed still further the peak on deposition decreased and approached a height approximately equal to the height on removal. It was also found that at first the rate of removal of the deposited material, as determined by the rate of change of activity, decreased with successive tests. Finally a stage was reached where the rate of removal was much smaller than at first but did not change for successive tests.

These results were interpreted in the following manner. At first the material coming from the thorium wire was not pure thorium. The percentage of foreign material decreased with time. The heights of peaks on deposition and the rates of removal were affected by the percentage of foreign material deposited. On removal, most of the foreign material evaporated at low temperatures and the height of the peak was approximately characteristic of pure thorium on tungsten. As the percentage of foreign material becomes negligible, the height of the deposition peak and the rate of removal approach values characteristic of pure thorium.

It was essential that the rate of deposition of thorium on different parts of the front surface of the ribbon be approximately the same. The effects of non-uniform deposition on the tungsten ribbon could be studied by noting the differences in activity of the ribbon as measured by the current to the different collectors. When only one or two spots on the thorium wire were clean, this effect was of course quite large. However, as the thorium wire was cleaned off, this effect decreased.

In each of the three tubes used, the object was to carry these preliminary treatments to the stage where the results for successive runs were consistent and did not change with continued aging of the tube. Actually this ideal stage was not reached in all cases. Filaments will break or burn out, especially thorium filaments. However, the ideal conditions were approximately reached in two of the tubes and the experimental data upon which the following analysis is based were all taken under conditions in which the various spurious effects described above were at least minimized and the ideal stage approximately reached.

Experimental Results on Tungsten Ribbon

The first problem was to determine from the experimental data how i, the electron emission in amperes per cm^2, measured at a fixed temperature (1274°K) and fixed applied field varies with the amount of thorium on the tungsten surface. Since i varies by such large factors, it is convenient to use log i rather than i. It was found that log i passed through a maximum as t, the time of glowing the thorium wire, progressed. Let t_m be the time required for log i to reach this maximum. As was to be expected, t_m decreased rapidly as the glowing temperature for the thorium wire increased. Furthermore it was found that if t/t_m was plotted in place of t, the results of various tests in which the thorium wire was glowed at different temperatures, could all be represented by a single curve. It is obvious that the maximum activity occurs at some critical, definite and reproducible amount of thorium on the surface of the tungsten, and that any amount on the surface can be expressed in terms of the amount corresponding to the maximum activity. We will therefore define a quantity f by the equation $f=t/t_m$. f is a measure of the amount of thorium on the tungsten surface. All of our results will be expressed in terms of f.

If the peak activity occurs at the time when just one layer of thorium atoms has been deposited on the tungsten ribbon, then f, as defined, is equal to the fraction of the surface covered or the number of layers on the surface of the tungsten ribbon. There is some evidence[7] that this is the case for caesium on tungsten. If subsequent work should definitely establish that the peak activity does not quite correspond to one layer, it will nevertheless be desirable to express amounts on the surface in terms of f because this quantity can be determined easily and precisely. Furthermore whenever the amount on the surface corresponding to the peak activity

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

is determined, f can very readily be converted to number of layers or number of atoms.

In order to determine the relation between log i and f, experimental values of log (i/i_m) were plotted against t/t_m. The plot was made for log (i/i_m), rather than log i, in order to compensate for small differences in the value of log i at the peak for different runs. Log i was determined by measuring the current to the central collector (C_2) on the side of the tungsten ribbon towards the thorium wire. This current was usually measured when the tungsten ribbon was maintained at a temperature of 1274°K. Measurements of i were made after each successive interval of glowing the thorium wire at a fixed temperature.

Fig. 2 is a plot of log (i/i_m) *vs.* t/t_m or f for several runs, taken after the thorium wire had reached a condition where the evaporation from the central part of the thorium wire was fairly uniform and the indications were that the peak on deposition was the same as the peak on removal.

The value of log (i/i_m) at $f=0$ was obtained by extrapolating a log $i-2$ log T *vs.* $1/T$ plot for the clean tungsten ribbon to $1/T=1/1274$. The values for log (i/i_m) for small f were not very accurate as the currents were small and almost at the limit of sensitivity of the galvanometer used. Beyond the peak the different runs diverge somewhat probably because of the different effects of non-uniformities on different runs.

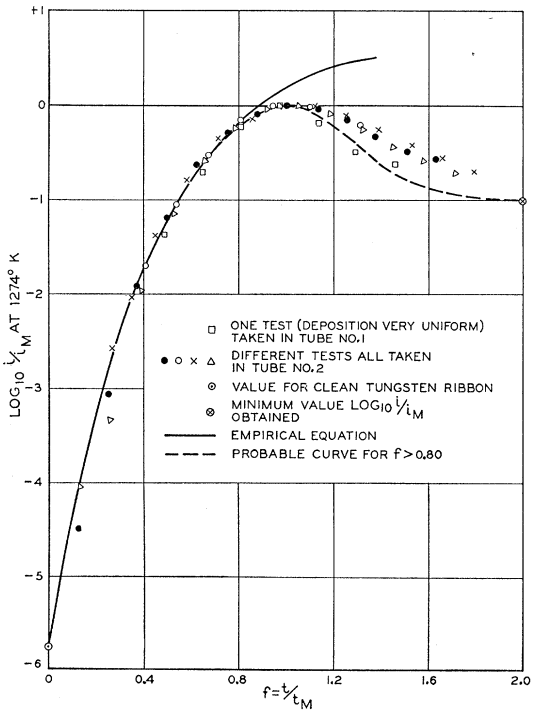

FIG. 2. The thermionic activity of the tungsten ribbon *vs.* the time of deposition from the thorium wire.

In order that the amount of thorium deposited on the ribbon be proportional to the time t, it is necessary that the evaporation rate from the thorium wire remain constant, and that no appreciable migration, evaporation or diffusion occur on the tungsten ribbon at the testing temperature. The first requirement was repeatedly tested and found to be satisfied. It was also found that the ribbon could be maintained at 1274°K for indefinite periods of time without changing the activity of the ribbon. Some tests were made by depositing the thorium on the ribbon while the ribbon was at room temperature. The ribbon was raised to 1274°K only for the short times necessary to test the activity. Other tests were made by maintaining the tungsten ribbon at 1274°K all the time. If appreciable migration, diffusion, or evaporation took place at 1274°K the resulting log i *vs.* time curves should have had different shapes. This, however, was not the case. Hence, the amount accumulated is proportional to t and likewise proportional to f.

It is to be noted here that log (i/i_m) is evidently not a linear function of f between $f=0$ and 1, and therefore log i is not a linear function of the amount of thorium on the tungsten surface.

For the case of barium on tungsten, Becker[8] found a log i *vs.* f curve very similar to that in Fig. 2. The relation between log i and f, for f from 0 to 0.8 or 0.9, was found to obey an empirical equation of the form

$$\log i = \log i_w + a(1-\epsilon^{-cf}), \qquad (1)$$

where a and c are constants, and i_w is the current from clean tungsten.

If this form of equation holds for Fig. 2, then we should have the following relation

$$\log (i/i_m) = \log (i_w/i_m) + a(1-\epsilon^{-cf}). \qquad (2)$$

The values of a and c which gave the best fit

[8] Becker, Phys. Rev. **33**, 1082 (1929).

were: $a=6.54$ and $c=2.38$. While an equation of the form of (2) probably holds if the current i is measured at some other testing temperature, the values of the constants a and c may be different. This question will be considered later.

The solid curve in Fig. 2 is a plot of log (i/i_m) *vs.* f as determined by Eq. (2) and these values of the constants. With the exception of a few points for small values of f, the empirical curve fits the experimental data quite well up to $f=0.8$. Since the experimental points for $f<0.3$ are quite inaccurate, as mentioned before, it can be said that the agreement between Eq. (2) and experiment is as good as the experimental accuracy. Except for differences in the values of the constants the same empirical relation between log i and f holds for both barium and thorium on tungsten for $f<0.8$.

The values of log (i/i_m) for f greater than 1 spread considerably because of non-uniformities in the deposition of thorium on the tungsten ribbon. The differences in amount of thorium deposited on different parts of the ribbon become greater as the time of deposition increases. Hence in this part of the curve even small non-uniformities in rate of deposition have quite an effect. It was found that log (i/i_m) approached a constant value for $f>2$. This constant value is indicated on Fig. 2 at $f=2.0$. A study of the influence of non-uniform deposition shows that beyond the peak the experimental points should lie above the true curve. Therefore, knowledge of this constant value of log (i/i_m) for $f>2$ and the general trend of the deposition curve, enables one to interpolate approximately for values of log (i/i_m) between f equal to 1 and f equal to 2. One has then as shown by the curve in Fig. 2 a relation between log (i/i_m) and f for thorium on a tungsten ribbon when the ribbon is at a temperature of 1274°K.

The average value of log i_m at 1274°K was determined from the experimental data. This value was log $i_m=6.08$–10. With this value, log i at 1274°K was plotted as a function of f as shown in Fig. 3.

The next step was to determine the relation between log i and T, the temperature, for various values of f and constant applied field. A Richardson plot can be made, even though the value of f for a particular surface condition may not be known. The procedure was to determine i for various values of T and constant f and then to plot log $i-2$ log T *vs.* $1/T$. Since these Richardson plots give straight lines they can be represented by an equation of the form

$$\log i-2\log T=\log A-b/2.3\,T, \qquad (3)$$

where log A and b are the intercept and slope respectively of a Richardson plot. The values of A and b are different for each straight line and therefore depend on f. The value of f for a particular straight line can be obtained by determining log i at 1274°K and consulting the data presented in Fig. 3. If A and b as functions of f were known, then log i as a function of f and T for constant applied field would be determined. Since the relation between log i at 1274°K and f is already known it is sufficient to determine b as a function of f or of log i at 1274°K. It is then possible to draw Richardson plots for any given value of f.

The procedure adopted was to determine log i at 1274°K, as well as b, from the various experimental Richardson plots; and then to plot b *vs.*

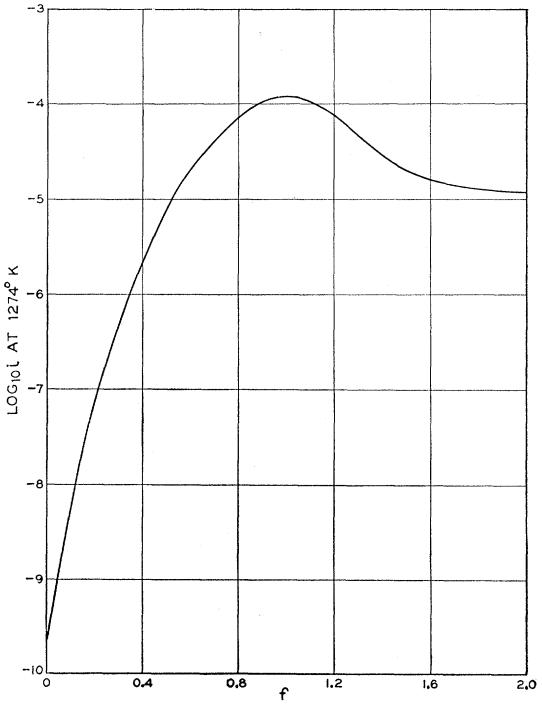

FIG. 3. Log$_{10}$ i at 1274°K *vs.* f; i expressed in amperes per sq. cm.

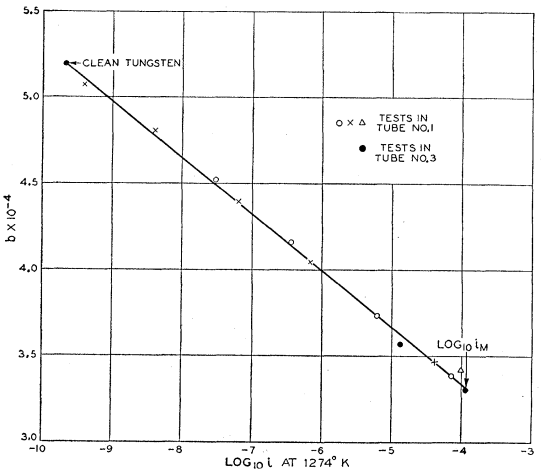

FIG. 4. b *vs.* $\log_{10} i$ at 1274°K. b is the slope of a Richardson plot in °K. i is the current in amp./cm².

$\log i$. Such a plot is shown in Fig. 4 for $f<1$. We have found such a plot advantageous because b is quite accurately a linear function of $\log i$ at 1274°K. For $f<1$, it follows that

$$b=b_w+\beta_1 \log (i/i_w)_{1274°K}, \tag{4}$$

where b_w is the value of b for the clean tungsten ribbon, and i_w is the electron emission for the clean tungsten ribbon. The symbol β_1 stands for the slope of the plot in Fig. 4 and is equal to -3.26×10^3.

It has been found that a relation can be developed between $\log (i/i_w)$ at any temperature and $\log (i/i_w)_{1274°K}$; and since $\log (i/i_w)_{1274°K}$ as a function of f is known, such a relation is the solution of this part of our problem. This relation can be developed as follows: For clean tungsten

$$\log i_w-2 \log T=\log A_w-b_w/2.3T. \tag{5}$$

Subtracting Eq. (5) from (3) for a particular value of T gives

$$\log \frac{i}{i_w}=\log \frac{A}{A_w}-\frac{b-b_w}{2.3T}. \tag{6}$$

This equation is general and holds true for all values of T in the experimental temperature range. For T equal to 1274°K, substitution of $b-b_w$ from (4) into (6) gives

$$\log \frac{A}{A_w}=\left(1+\frac{\beta_1}{2.3\times1274}\right)\log\left(\frac{i}{i_w}\right)_{1274°K}. \tag{7}$$

Now by using (6) for any temperature, let us substitute values of $b-b_w$ and $\log (A/A_w)$ from (4) and (7) in (6). We have as a result

$$\log\left(\frac{i}{i_w}\right)_T=\left[1+\frac{\beta_1}{2.3}\left(\frac{1}{1274}-\frac{1}{T}\right)\right]\log\left(\frac{i}{i_w}\right)_{1274}. \tag{8}$$

This Eq. (8) gives $\log (i/i_w)$ at any temperature in terms of $\log (i/i_w)$ at 1274°K. Since (4) only holds for $f<1$ Eq. (8) is only valid for that range.

It was found that an equation of the form

$$b=b_m+\beta_2 \log (i/i_m)_{1274} \tag{9}$$

also held for $f>1$ where b_m and i_m are the values of b and i for $f=1$, and $\beta_2=-4.82\times10^3$. We can then by a similar analysis arrive at the equation

$$\log\left(\frac{i}{i_w}\right)_T=\left[1+\frac{\beta_2}{2.3}\left(\frac{1}{1274}-\frac{1}{T}\right)\right]\log\left(\frac{i}{i_w}\right)_{1274}+\frac{\beta_1-\beta_2}{2.3}\left(\frac{1}{1274}-\frac{1}{T}\right)\log\left(\frac{i_m}{i_w}\right)_{1274} \tag{10}$$

which is valid for $f>1$.

In order to use Eqs. (8) and (10) it is necessary to know the values of $\log i_w$ and $\log i_m$ at 1274°K. The value of $\log i_m$ has already been given; it is 6.08–10. The electron emission per sq. cm from the clean tungsten ribbon was determined several times. Analysis gave $b_w=5.20\times10^4$°K and $\log A_w=1.84$ or $A_w=69$ amp. per cm² per deg.². From these values, $\log i_w$ at 1274°K was computed and found to be 10.32–20. The value for b_w obtained compares quite well with the accepted value 5.24×10^4°K for clean tungsten.

An interesting consequence of Eq. (4) or Eq. (8) is that the family of Richardson lines for thorium on tungsten ($0<f<1$) all have a common intersection point. This intersection point occurs

at the value of T for which $\log (i/i_w)_T$ is equal to zero. On solving Eq. (8) for the value of T that satisfies this condition we obtain $T=12{,}500°K$. If this intersection point had occurred at a value of $1/T$ equal to zero then the values of A for all the Richardson lines would have been the same. For this to be true it would be necessary that β_1 have the value -2.93×10^3 instead of -3.26×10^3.

In a similar way it follows from Eq. (9) that for $f\geq1.0$ all Richardson lines have a common intersection point at an extrapolated temperature of 3250°K. Hence for $f\leq1.0$ all Richardson lines cross the clean tungsten line at a common point for which $1/T=8.00\times10^{-5}$ or $T=12{,}500°K$ while for $f\geq1.0$ all Richardson lines cross the line for $f=1.0$ at a common point for which $1/T=3.08\times10^{-4}$ or $T=3250°K$.

Equations (8) and (10) enable one to calculate $\log (i/i_w)$ for any value of T and f provided the relation between $\log (i/i_w)_{1274}$ and f is known. This analysis therefore has determined the activity as a function of the two independent variables, temperature and amount of thorium on the tungsten surface for constant applied field.

The validity of Eqs. (8) and (10) may be tested by using them to determine Richardson lines and comparing these with experimentally determined ones. Such a comparison for $f<1$ is shown in Fig. 5 where the points represent actual experimental determinations and the lines are determined from Eq. (8). The comparison for $f>1$ is shown in Fig. 6. It is apparent that the empirical formulae give results in good agreement with actual experimental determinations for all values of f which have been investigated. In Fig. 7 a graded series

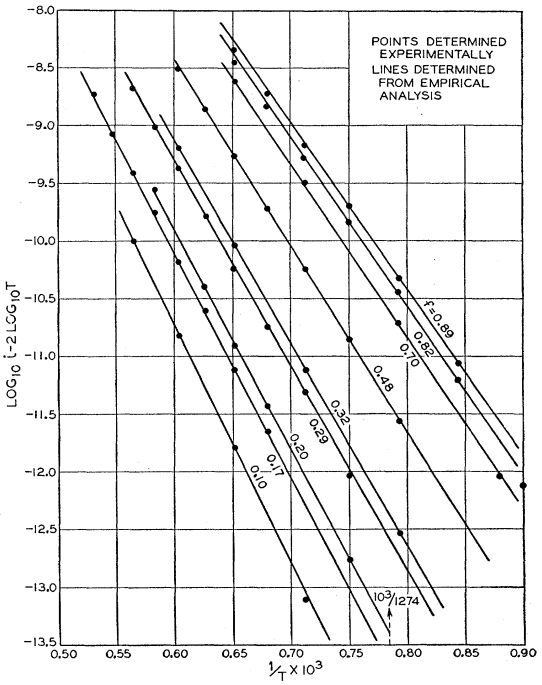

FIG. 5. Richardson plots for various amounts of thorium on tungsten; $f<1.0$.

of Richardson lines is given for f in the range 0 to 1.

For the range of f from 0 to 0.8 for which Eq. (2) holds we can substitute for $\log (i/i_w)_{1274}$ in terms of f in Eq. (8).

From Eq. (2) we have

$$\log (i/i_w)_{1274}=6.54(1-\epsilon^{-2.38f}). \qquad (11)$$

Substitution of this value of $\log (i/i_w)_{1274}$ in Eq. (8) gives

$$\log\left(\frac{i}{i_w}\right)_T=6.54\left[1-1.42\times10^3\left(\frac{1}{1274}-\frac{1}{T}\right)\right](1-\epsilon^{-2.38f}). \qquad (12)$$

This equation gives $\log (i/i_w)$ at any temperature in terms of f. We see therefore that $\log (i/i_w)$ at any temperature is given by an equation of the form

$$\log (i/i_w)_T=a'(1-\epsilon^{-c'f})$$

where c' is a constant equal to 2.38 while a' depends on temperature and is given by

$$a'=6.54[1-1.42\times10^3(1/1274-1/T)].$$

We will have occasion to use the expression

$$[(\log i-\log i_w)/(\log i_m-\log i_w)]_T$$

in terms of $\log (i/i_w)_{1274}$. This relation can be developed from the preceding equations and the result is

$$\left(\frac{\log i-\log i_w}{\log i_m-\log i_w}\right)_T=\frac{1}{\alpha}\log\left(\frac{i}{i_w}\right)_{1274}$$

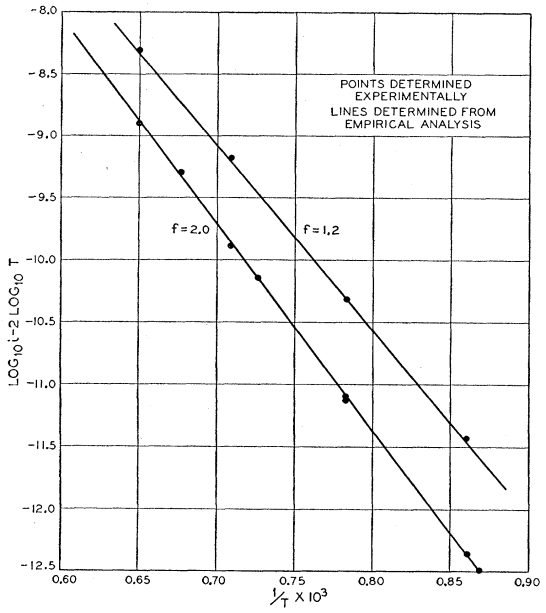

FIG. 6. Richardson plots for thorium on tungsten; $f>1.0$.

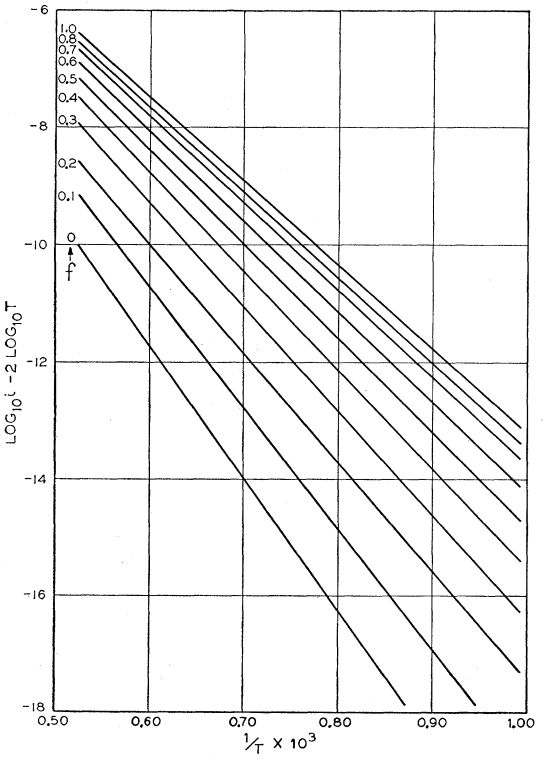

FIG. 7. A graded series of Richardson plots for $0<f<1.0$; applied potential 100 volts.

where α is $(\log i_m/i_w)_{1274}$, and is equal to 6.08–10–(10.32–20) or 5.76.

For the range of f from zero to 0.8 we have then that

$$\left(\frac{\log i-\log i_w}{\log i_m-\log i_w}\right)_T=\frac{a}{\alpha}(1-\epsilon^{-cf}), \qquad (13)$$

where $a=6.54$, $c=2.38$ and $a/\alpha=6.54/5.76=1.13$. Since a/α and c are constants independent of temperature, the function on the left side of Eq. (13) is also independent of T and the subscript T can be omitted. Let θ represent this function.

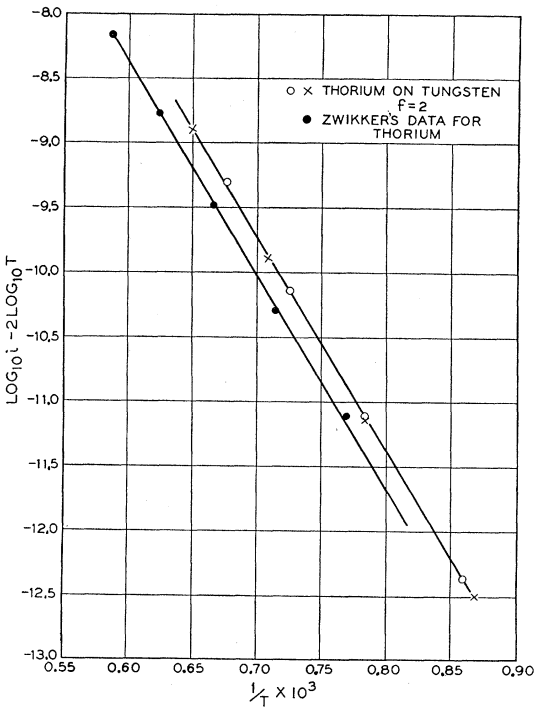

FIG. 8. Comparison of Richardson plots for thorium and for thorium on tungsten, $f=2.0$.

It is of interest to compare the values of emission from the tungsten ribbon when f is greater than 2 with the emission from clean thorium as determined by Zwikker.[9] Fig. 8 shows a plot of $\log i-2\log T$ *vs.* $1/T$ as determined for $f=2$ and as determined for clean thorium by Zwikker. While the values for $\log i-2\log T$ for f approximately 2 on the ribbon are

[9] Zwikker, Proc. Amst. Acad. Sci. **29**, 792 (1926).

a factor of 2 larger than Zwikker's values for clean thorium it is somewhat surprising that such a small amount of thorium on tungsten will give a surface whose thermionic characteristics are approximately the same as those of a clean thorium surface.

The results thus far are summed up in Table I

TABLE I. *Summary of numerical results.*

f	θ	$b\times10^{-4}$	A	log i_{1274}	log$(i/i_w)_{1274}$
0	0	5.20	69	0.32–10	0
0.1	0.24	4.75	48	1.71–10	1.39
0.2	0.43	4.39	36	2.80–10	2.48
0.3	0.58	4.11	29	3.66–10	3.34
0.4	0.70	3.89	24	4.34–10	4.02
0.5	0.79	3.71	21	4.88–10	4.56
0.6	0.86	3.58	19	5.30–10	4.98
0.7	0.92	3.46	17	5.65–10	5.33
0.8	0.97	3.39	16	5.86–10	5.54
0.9	0.99	3.34	15.6	6.02–10	5.70
1.0	1.00	3.32	15.5	6.08–10	5.76
1.2	*	3.43	20	5.87–10	5.55
1.4		3.61	37	5.46–10	5.14
1.6		3.74	53	5.20–10	4.88
1.8		3.79	61	5.11–10	4.79
2.0		3.80	65	5.07–10	4.75

* θ not defined for $f>1$.

which gives corresponding values of f, θ, b, A, $(\log i)_{1274}$ and $\log (i/i_w)_{1274}$.

COMPARISON WITH THORIATED TUNGSTEN

It is interesting to compare these results with those obtained for thoriated tungsten wire. As Langmuir[1] has shown, thorium can be brought to the surface of a thoriated tungsten wire by diffusion from the interior. The steps in such an activation process are: The wire is first glowed at approximately 2800°K in order to reduce thorium oxide to metallic thorium and to clean the surface of the wire. The wire is quickly cooled. It is then kept at an activating temperature, 1800 to 2200°K, for various intervals of time in order to allow thorium to diffuse to the surface. After each such interval, the activity is tested by measuring the electron emission at some fixed testing temperature at which the activity does not change with time. Most of the adsorbed thorium can subsequently be removed by flashing the filament at a high temperature, such as 2600°K for a short time.

Fig. 9 gives the results of two such tests on the 4 mil thoriated tungsten wire marked C in Fig. 1. The testing temperature was 1549°K in both tests. Log (i/i_m) at 1549°K was plotted against t, the time of activation. For run 1, the activation temperature was 1940°K, and for run 2 it was 1845°K. Except for the difference in rate of activation, the curves are quite similar: Both curves go through a maximum and then approach an equilibrium activity. The equilibrium activity for the run at 1845°K was definitely lower than that at 1940°K.

From our previous results it is possible to determine for these tests how f varies with the time of activation. The curve for f *vs.* log (i/i_m) at 1549°K can be obtained from Figs. 5 and 6. Values of f for each value of log (i/i_m) corresponding to various values of t in Fig. 9, can be determined. In Fig. 10, f has been plotted against time of activation for the two runs in Fig. 9. It is seen that for some time f increases linearly with the time; then it increases more and more slowly until it approaches a constant value. The rate of increase of f with time is greater for the run at 1940°K while the final constant value approached by f is greater for the run at 1845°K. It is to be noted that f is not zero when t is zero. This is to be expected since the thoriated tungsten wire may not be completely clean at 2800°K and should activate somewhat on cooling from 2800°K.

From these results we draw the following conclusions: Thorium diffuses to the surface at a rate which is constant for a particular run; this rate depends on the activation temperature and on the amount and distribution of thorium in the tungsten. At first, the rate of evaporation of thorium from the surface is negligible, so that the amount of thorium accumulated increases linearly with time. As the surface concentration of thorium increases, the rate of evaporation increases rapidly.[10] When the evaporation becomes comparable with the diffusion rate, the rate of accumulation of thorium on the surface is no longer equal to the rate of diffusion, but gets less and less until equilibrium is reached between evaporation and diffusion. The rate of evaporation increases more rapidly with temperature

[10] It will be shown later that the rate of evaporation of thorium from a tungsten surface is an exponential function of the amount on the surface.

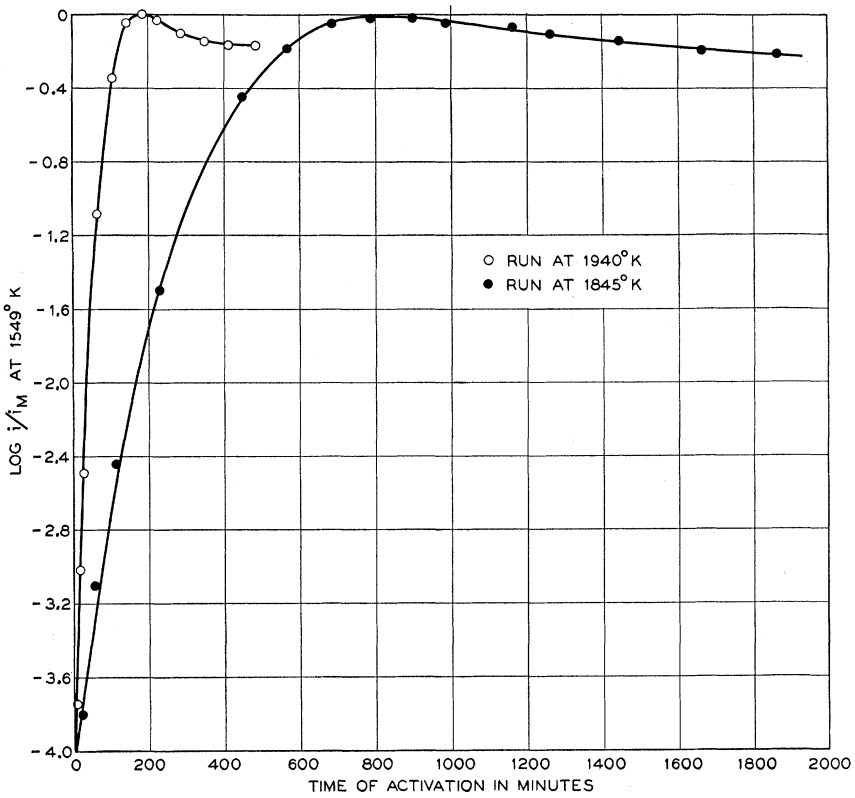

FIG. 9. Activation curves for thoriated tungsten wire.

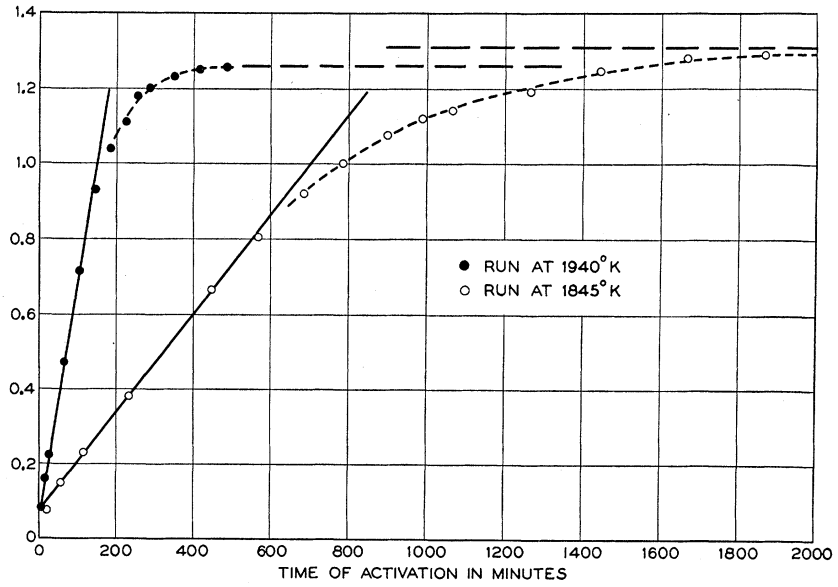

FIG. 10. *f vs.* time of activation for data shown in Fig. 9.

than the rate of diffusion, and therefore as the activation temperature increases, the equilibrium value of f decreases. Numerous subsidiary experiments showed that if the activation temperature is high enough, the equilibrium value of f is less than 1.0.

One would expect that the dependence of log i on temperature should be the same for a thoriated tungsten wire as it is for the tungsten ribbon when the value of f for the two surfaces is the same. If, therefore, we make a plot of b *vs.* log i at 1274°K from experimentally determined values for thoriated tungsten wire and compare it with the similar plot for the tungsten ribbon (Fig. 4), the two should agree. In Fig. 11, such a comparison is shown. The dashed line represents the results for the ribbon and is taken from Fig. 4. For the case of thoriated tungsten we have the plotted points determined from Dushman's[3] data and some points obtained by analyzing the data that we have taken on thoriated tungsten. While all the points obtained for thoriated tungsten lie approximately on a straight line this straight line does not quite agree with the one determined for the ribbon. In analyzing the results shown in Fig. 11 it is to be noticed that the value that Dushman determined for log i_m does not quite agree with the value we obtained for thoriated tungsten. Note the largest values of log i for which points are given from our data and Dushman's data. It was found that this difference might be explained by a difference in temperature scale as a shift in temperature scale will change the values of both log i at 1274°K and b in such a way that points still lie approximately on the same line.

This comparison shows that our results for thoriated tungsten agree with Dushman's results except for a possible difference in temperature scale and that the combined results for thoriated tungsten do not agree exactly with our results for thorium on the tungsten ribbon. Since the tungsten ribbon is different from the thoriated tungsten wire in that the wire contains thorium oxide and that as a result of this thorium oxide the wire has a much smaller crystal size it may be reasonable to suppose that the differences shown in Fig. 11 are due either to the difference in crystal size of the two filaments or to the direct effects of the presence of thorium oxide in the wire.

Comparison with Langmuir's Results

Since our work leads to an interpretation which in some respects is radically different from that of Langmuir and others who have followed his method, it seems desirable to discuss this work. In comparing Langmuir's results with our own, it is necessary to compare his θ with our f. While Langmuir[1] defines θ as "the fraction of the surface covered by thorium atoms," all of his numerical values of θ are based on a theory from which it follows that "the logarithm of the emission is a linear function of θ so that θ may be calculated from the equation[11]

$$\theta=(\log i-\log i_w)/(\log i_m-\log i_w).\text{"} \qquad (14)$$

So far as we know, no derivation of this equation has been published. Langmuir and others have, nevertheless, used this equation in the calculation of evaporation rates, diffusion rates, heats of evaporation and heats of diffusion. We have shown that this formula is not in agreement with experiment. Hence numerical quantities based on it are generally erroneous. Furthermore, it has led to certain false concepts with regard to the mechanism of adsorption.

At first sight, it might appear that Langmuir's experimental data differ from ours; but this is not the case, as can be shown in the following two ways:

Fig. 12 is a plot of f *vs.* time of activation for an activation run taken from Langmuir's data at 2000°K. For comparison, we have plotted the results of our run at 1940°K, previously shown in Fig. 10. It is seen that Langmuir's results are quite similar to our own. They differ somewhat in that the diffusion rate at 2000°K in Langmuir's case was less than the diffusion rate we obtained at a lower temperature, 1940°K; also, the equilibrium value of f in his case was 1.0 or slightly less, while in our case it was greater than 1.2. It is to be expected that the diffusion rate should depend upon the concentration of thorium in the wire and should consequently vary from one wire to the next. Since, in Langmuir's case, the rate of diffusion is less than in ours, and since the rate of evaporation is higher, because of the higher

[11] This function is the same as the left side of Eq. (13) which we have designated by θ.

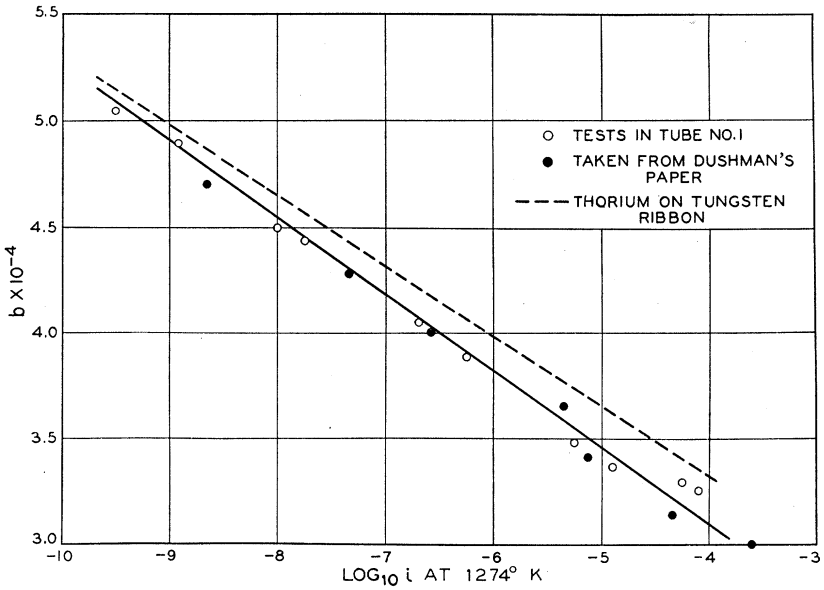

FIG. 11. b *vs.* $\log_{10} i$ at 1274; b in °K and i in amp./cm².

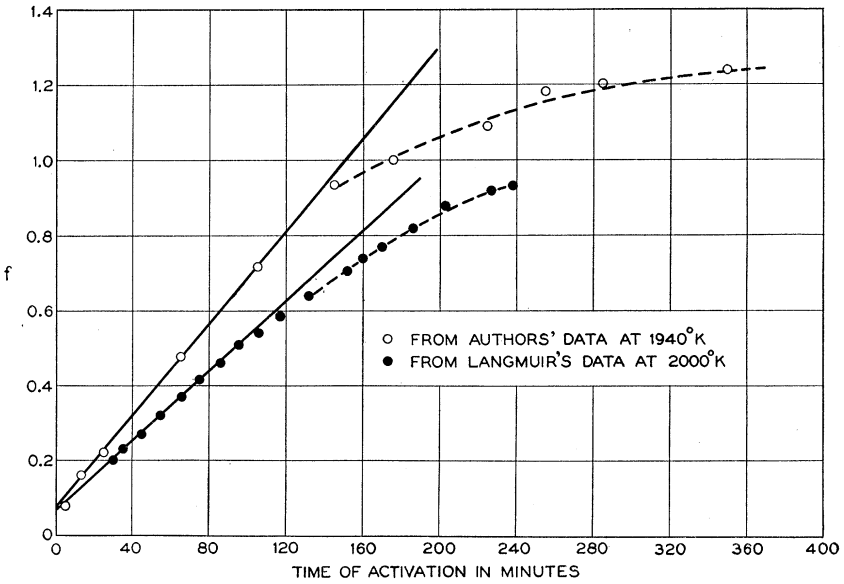

FIG. 12. f *vs.* time of activation—comparison of Langmuir's and author's data.

temperature, his equilibrium value of f should be lower; and it is.

The second proof that Langmuir's experimental results yield a log i *vs.* t curve agreeing with our own, is based on Langmuir's empirical equation[1]

$$d\theta/dt = k(1-\theta). \tag{15}$$

The solution of this differential equation is

$$\theta = 1-\epsilon^{-kt} \tag{16}$$

since $\theta = (\log i - \log i_w)/\alpha$, where $\alpha = \log i_m - \log i_w$, it follows that Langmuir's experimental results are given by the equation

$$\log i = \log i_w + \alpha(1-\epsilon^{-kt}), \qquad (17)$$

which is of the same form as our empirical Eq. (1).

It is clear then, from Langmuir's experiments as well as our own, that log i is not a linear function of t. Langmuir explains this departure from linearity by his principle of "induced evaporation," which states that whenever a thorium atom diffuses to the surface from the interior of the tungsten at a spot which is already occupied by a thorium atom, it "induces" this atom to evaporate. Consequently, the rate of accumulation of thorium should not be constant, but should be proportional to the fraction of the surface which has not yet been covered, i.e., to $(1-\theta)$. In this way, Langmuir accounted for his empirical relation given in Eq. (15) and for the nonlinearity of the log i *vs.* t curve.

In contrast with this, we believe that the principle of induced evaporation is not applicable in any case similar to thoriated tungsten, for the following two reasons. As will be shown later, thorium atoms migrate on the surface of tungsten at temperatures which are even lower than activating temperatures, and migration can be brought about without any appreciable evaporation. Consequently, if a thorium atom ever does diffuse to the surface just underneath another thorium atom, it will push this atom aside rather than "induce" it to evaporate. In other words the tendency would be for the thorium atoms to distribute themselves over the surface rather than to leave it. In the second place, Clausing[12] has shown that thorium diffusion does not occur through the tungsten lattice, but between the boundaries of the tungsten crystals. Consequently the only way in which the surface can be covered with thorium is by migration from the grain boundaries, and the rate of accumulation of thorium on the surface should not be proportional to the amount of bare surface, $(1-\theta)$. Now the only evidence presented by Langmuir for induced evaporation of thorium from tungsten is that on his view the rate of accumulation is proportional to $(1-\theta)$. Hence Clausing's work also shows that the induced evaporation hypothesis is not in accord with the experimental facts.

[12] Clausing, Physica **7**, 193 (1927).

What then is to be inferred from the nonlinearity of the log i *vs.* t, or *vs.* f, curve? We have always maintained that this nonlinearity means that the effectiveness of an individual electropositive atom in reducing the work function of the surface is not constant, but decreases as f increases.[13] This in turn must mean that the fraction of the adsorbed thorium which is ionized or, if one prefers, the average electric moment of a thorium adatom, decreases with the surface concentration. In this connection, it is interesting to note that in his most recent work,[14] Langmuir apparently accepts this interpretation for caesium and barium on tungsten.

Langmuir's activation curves for thoriated tungsten never pass through a maximum. The reason, undoubtedly, is that his activation temperatures were too high for the maximum to appear. If the activation temperatures are low enough, or if thorium is deposited from an external source, the maximum always appears.

The following equations will be found useful in comparing Langmuir's numerical values with our own. It was shown above that the relationship between log i and f is given by Eq. (2) for $f<0.8$. This range is approximately the same as that for which Langmuir claims his equation (Eq. (15)) holds. It follows from Eq. (13) that

$$\theta = (a/\alpha)(1-\epsilon^{-cf}) \qquad (18)$$

where $\alpha = \log i_m - \log i_w$, and that

$$\frac{d\theta}{dt} = \frac{ac}{\alpha}\epsilon^{-cf}\frac{df}{dt} = \frac{ac}{\alpha}\left(1-\frac{\alpha}{a}\theta\right)\frac{df}{dt}. \qquad (19)$$

By means of the last equation, it is possible to convert Langmuir's evaporation rates in terms of $d\theta/dt$ to the true evaporation rates in terms of df/dt. The comparison of evaporation data will be discussed later.

This discussion may be summarized as follows: Everyone agrees that when a thoriated tungsten filament is activated, log i does not increase linearly with the time of activation. Langmuir interprets this nonlinearity as evidence for

[13] J. A. Becker, see Phys. Rev. **28**, 341 (1926), Trans. Am. Electro-Chem. Soc. **55**, 153 (1929) and Faraday Society Symposium on Adsorption, January, 1932.

[14] Langmuir, J. Am. Chem. Soc. **54**, 2798 (1932). See particularly p. 2820.

induced evaporation and for the correctness of his formula which states that log i increases linearly with the amount of surface covered. On the other hand, we present new evidence which shows that the rate of accumulation of thorium on the surface is directly proportional to the time and conclude that log i does not vary linearly with the amount of adsorbed thorium. From this nonlinearity we conclude that the electrical moment per atom decreases as the number of adatoms increases. Hence it is no longer necessary to assume induced evaporation. Furthermore, the evidence of surface migration and Clausing's[12] work which shows that thorium diffuses along grain boundaries rather than through the body of the tungsten crystals, lead to the conclusion that induced evaporation does not exist.

Dependence of Emission on Applied Field

All measurements of the current from the tungsten ribbon were made with an applied potential of 100 volts between it and the surrounding electrodes. As pointed out in the introduction the activity of the ribbon depends on the applied field. For example when the tungsten surface was clean, ($f=0$), reducing the applied potential from 100 volts to 10 volts reduced the thermionic current by approximately 15 percent. For $f=0.7$ and $f=2.0$ the corresponding reductions in currents were respectively 25 and 15 percent. It was not feasible to make a detailed study of these effects for the tungsten ribbon since the field is not uniform over the surface of the ribbon. It is quite probable that the exact dependence of the activity on applied field will be characteristic of the particular filament used rather than being characteristic for thorium on tungsten. Moreover, the significant point here is that the dependence of activity on applied field is so small in comparison to the dependence on f and T that the exact field used will not greatly affect the conclusions.

The study of the dependence of activity on applied field is a problem in itself and is really beyond the scope of this paper. However, in this connection some data were taken on the 4-mil thoriated tungsten filament. For this filament the field is uniform and is directly proportional to the applied potential; and the dependence of emission current on plate potential was found to be much more pronounced than in the case of the tungsten ribbon. The results can be summarized most conveniently by determining how the parameters A and b vary with the applied potential. For an amount of thorium on the tungsten surface such that $f=0.6$ it was found that both A and b decreased as the potential was increased. For $f=1$ it was found that A was approximately constant and independent of the potential and that the change in b with potential was much less than it was at $f=0.6$. The dependence of A and b on applied potential was most pronounced in the region for f from 0.3 to 0.6. These results are shown in Figs. 13 and 14. There were only comparatively few data available with which to make the calculations. The results therefore are only approximate and it would be necessary to make a more thorough investigation before final conclusions could be reached. The absolute values of b are not accurate and therefore the values for log A are approximate since a small error in b can make a large error in the value of log A. However, relative values of b and of log A should be quite reliable.

Evaporation of Thorium from Tungsten

We can now proceed to study the rate of evaporation of thorium from tungsten for various values of f at one or more temperatures. Results have been obtained for a range of f from 0.05 to 0.9 at a temperature of 2200°K. These results were obtained in the following manner. First several layers of thorium were deposited on one side of the tungsten ribbon. In order to determine the rate of removal of thorium from the tungsten it was essential to eliminate the effect of removal from the front due to migration of the thorium to the back of the tungsten ribbon. The discussion of migration will be taken up later. It is sufficient here to state that the thorium on the front was uniformly distributed over the surface of the ribbon by migration. The thorium was then removed from both sides by flashing the ribbon for successive intervals at 2200°K. Between each interval the activity of the tungsten ribbon was measured at some low testing temperature. This sufficed to determine the amount on the surface (f) as a function of the time of flashing at 2200°K. Then $\Delta f/\Delta t$ in layers per sec. was calculated for various values of f. In Fig. 15 is

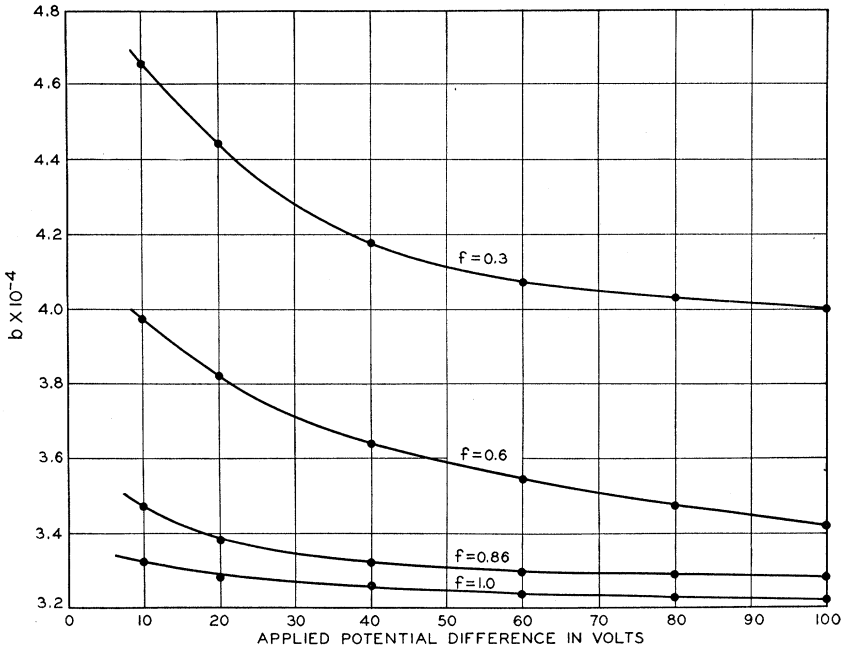

FIG. 13. Dependence of b on applied potential for thoriated tungsten wire.

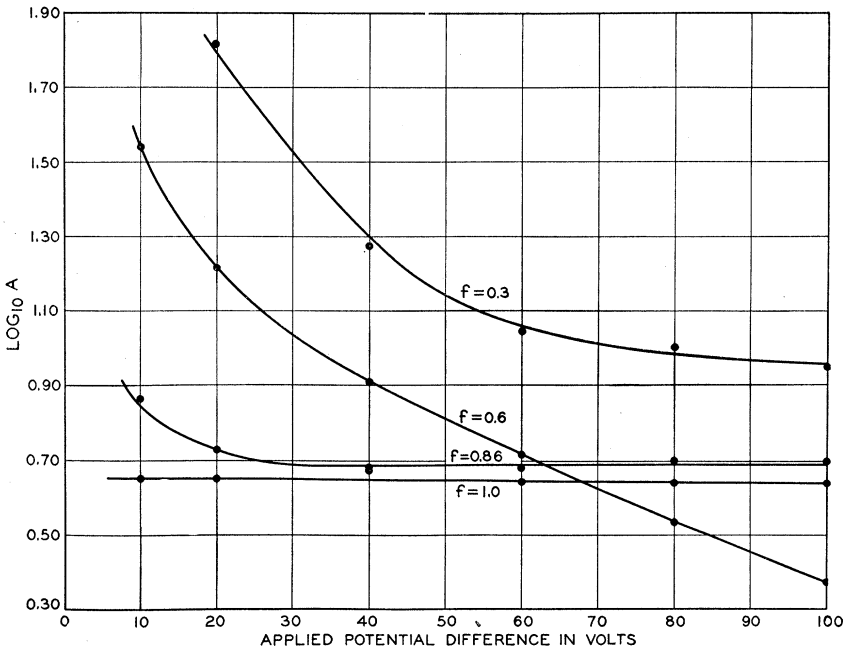

FIG. 14. Dependence of A on applied potential for thoriated tungsten wire.

shown a plot of log $(\Delta f/\Delta t)$ *vs.* f. Between $f=0.2$ and $f=0.9$, log $(\Delta f/\Delta t)$ is approximately a linear function of f. Therefore $\Delta f/\Delta t$ is an exponential function of f. For f less than 0.2, log $(\Delta f/\Delta t)$ falls off more rapidly.

When one attempts to see the significance of the main features of Fig. 15, one is led to the

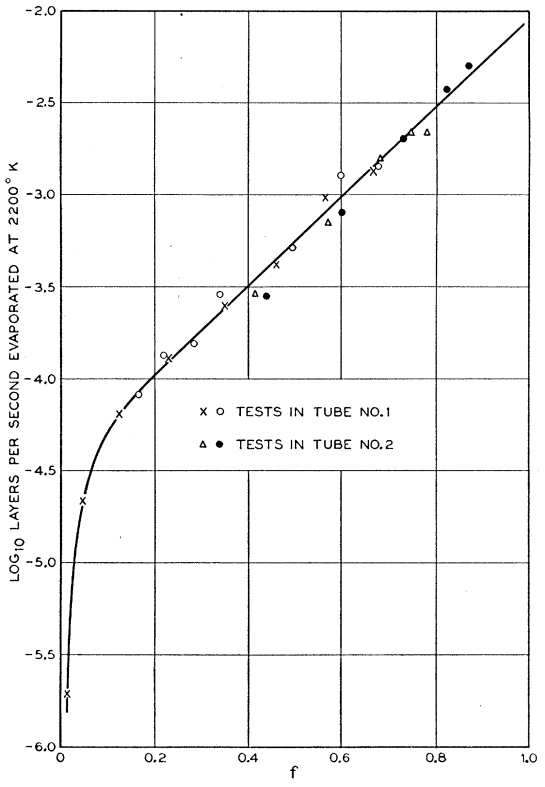

FIG. 15. Rate of evaporation of thorium from tungsten ribbon at 2200°K *vs.* f.

consideration of the factors that should determine the rate of evaporation of adatoms (E_a). It has been proposed[13] that E_a is given by an equation of the form

$$E_a=\Delta f/\Delta t=KT^n f\epsilon^{-w/T},$$

in which K is a constant, n is a small number, and w represents the work function for evaporation of adatoms. The work function w very likely depends on f and may also depend on the temperature T. The factor f is introduced since it is to be expected that the number of atoms which evaporate should be proportional to the number on the surface as well as to the probability that an individual atom evaporates. If E_a, for thorium on tungsten, is given by an equation of this form, a plot of log $[(1/f)(\Delta f/\Delta t)]$ *vs.* f might be expected to yield a curve which would no longer show the steep rise shown in Fig. 15 for small values of f. Fig. 16 shows such a plot. For a complete analysis of the dependence of the evaporation rate on f and T it would be necessary to have evaporation data at other temperatures. However from the fact that $(1/f)(\Delta f/\Delta t)$ increases with f it follows that the work to remove a thorium atom from the tungsten surface decreases as the number of thorium atoms on the surface increases.

Since it is possible for some of the thorium to diffuse into the tungsten ribbon, $\Delta f/\Delta t$ represents the sum of the rates of diffusion and evaporation. If the rate of diffusion is not negligible, then $\Delta f/\Delta t$ should depend on the concentration of thorium in the tungsten. The concentration in the tungsten should in turn depend on the treatment given the tungsten ribbon between successive tests. As mentioned before in the preliminary treatment of the tube, the rate of removal at first decreased with each successive test. However, this behavior was most likely due to foreign material coming from the thorium wire, rather than to diffusion of thorium into the tungsten ribbon. After the preliminary treatment was more or less complete the rate of removal became independent of the previous treatment of the ribbon. There was then no evidence leading to the conclusion that the rate of removal depended on the time of flashing the tungsten ribbon between successive tests. Furthermore, if the concentration of thorium in the tungsten is appreciable, then after the tungsten ribbon is cleaned off by glowing at 2200°K, it should activate on glowing at some lower temperature. This was tried but no evidence of activation was obtained. The conclusion then is that the rate of diffusion into the tungsten was small compared to the rate of evaporation at 2200°K. Examination of the ribbons after removal from the tube has shown that the ribbons are made up of several large single crystals. If appreciable diffusion can take place only along grain boundaries,[12] then diffusion of thorium into the ribbon should be small.

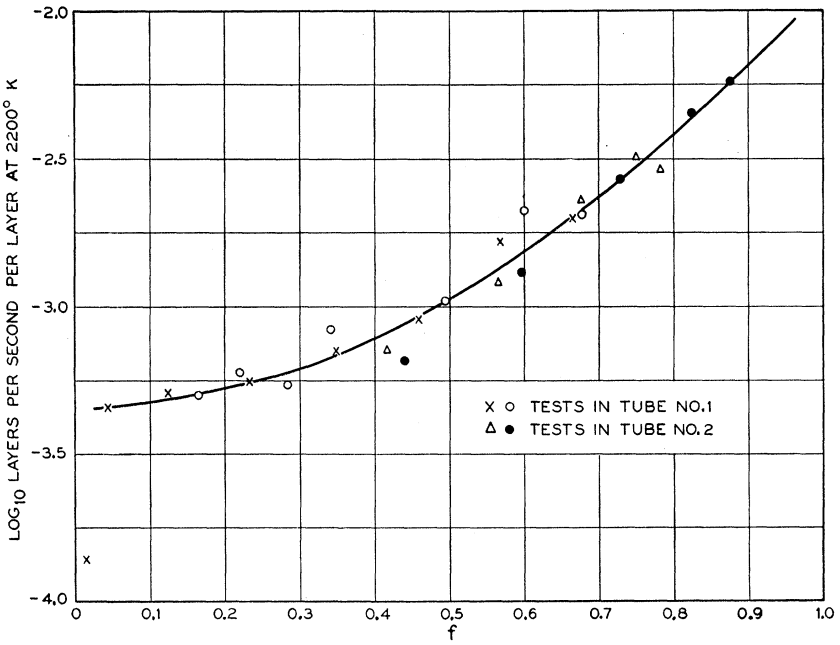

FIG. 16. Rate of evaporation per layer at 2200°K *vs.* f.

Langmuir's[1] and Andrew's[15] results on evaporation of thorium from tungsten are not directly comparable with our results because their results are given in terms of the parameter θ. It is, however, possible to convert their results to the same basis as ours.

From Eq. (19) we have

$$\frac{df}{dt}=\frac{1}{c(a/\alpha-\theta)}\frac{d\theta}{dt}=\frac{0.368}{(1-0.88\theta)}\frac{d\theta}{dt}. \quad (20)$$

If we substitute for $d\theta/dt$ in (20) values of E/N_0 from Langmuir's data or values of $2.3\theta d(\log_{10}\theta)/dt$ from Andrew's data we obtain corresponding values of df/dt in layers per sec. for particular values of θ or for particular values of f.

In Fig. 17 we have plotted the results of such a conversion. The curves give values of $\log_{10}(df/dt)$ as a function of f where df/dt represents the evaporation rate in layers per sec. at 2200°K. The data for curve 1 was obtained from Andrew's results. Curve 2 was obtained from Langmuir's results. Curve 3 represents our own results. Curve 4 is taken from some unpublished data obtained by J. M. Eglin at these laboratories. Eglin studied the rate of evaporation from a 4-mil thoriated tungsten wire by measuring the rate of deposition of the evaporated thorium on a tungsten ribbon. All the curves agree approximately as to shape and trend. The values of df/dt vary by more than a factor of ten. If this discrepancy is due to differences in temperature scales used, a spread of 50° from the mean would be sufficient to explain the differences. Considering that 50° is less than 3 percent of 2200°K, this explanation is not improbable. The ranges of f which the various data cover are indicated approximately by the extent of the curves.

MIGRATION OF THORIUM ON TUNGSTEN

For caesium[7] and for barium[16] on tungsten it has been shown that the adatoms move about or migrate over the surface. In this section we will show that thorium adatoms migrate over the surface; that the rate of migration increases rapidly with temperature, and that the rate of migration is appreciable at temperatures so low that evaporation is negligibly small. From a detailed study of this process we can obtain additional evidence that the parameter f is indeed a correct measure of the surface concen-

[15] Andrews, Phys. Rev. **33**, 454 (1929).

[16] Becker, Trans. Am. Electro-Chem. Soc. **55**, 153 (1929).

tration. It is also possible to draw some conclusions in regard to the nature of the mechanism involved in the migration process. This mechanism it appears is different from that involved in the ordinary case of diffusion in which the diffusion coefficient is independent of the concentration. On the other hand, it can be deduced that some of the migration, and perhaps most of it, is caused by atoms which rise above the surface at one point and return to it at another point. A preliminary value for the heat of migration is found to be 110,000 calories per mol.

The study of migration of thorium on the surface of the tungsten ribbon offers another means of testing whether or not the parameter f is proportional to the amount on the surface. Suppose for example we cover just one side of the tungsten ribbon until the current per sq. cm from this side has a given value at a given testing temperature. This value determines a value of f for this side of the ribbon, and f for the reverse side is zero. If now the thorium initially on one side of the ribbon can be uniformly distributed over both sides by migration then the emission per sq. cm from both sides should be the same. If this can be done at a temperature so low that appreciable thorium is not lost by evaporation, then the original amount of thorium should be distributed over twice the area. Therefore, if f is proportional to the fraction of the surface covered, the value of f as determined by the new value of emission per sq. cm should be just half of the original value of f.

In order to study migration, a given amount of thorium was first deposited on the side of the tungsten ribbon towards the thorium wire; then the tungsten ribbon was flashed for successive intervals at low temperatures such that no appreciable evaporation took place. The activity of each side of the tungsten was measured after each interval of flashing. The plot in Fig. 18 is based on a typical test. In the previous deposition of thorium on tungsten, the total time of deposition was 11.25 hours and the time at which the maximum activity occurred was 6.35 hours. The value of f on this side of the ribbon at the start of the migration test was 11.25/6.35 or 1.77. The tungsten ribbon was then flashed for definite intervals of time at 1535°K. Fig. 18 shows the plot of log (i/i_m) as measured at 1261°K after

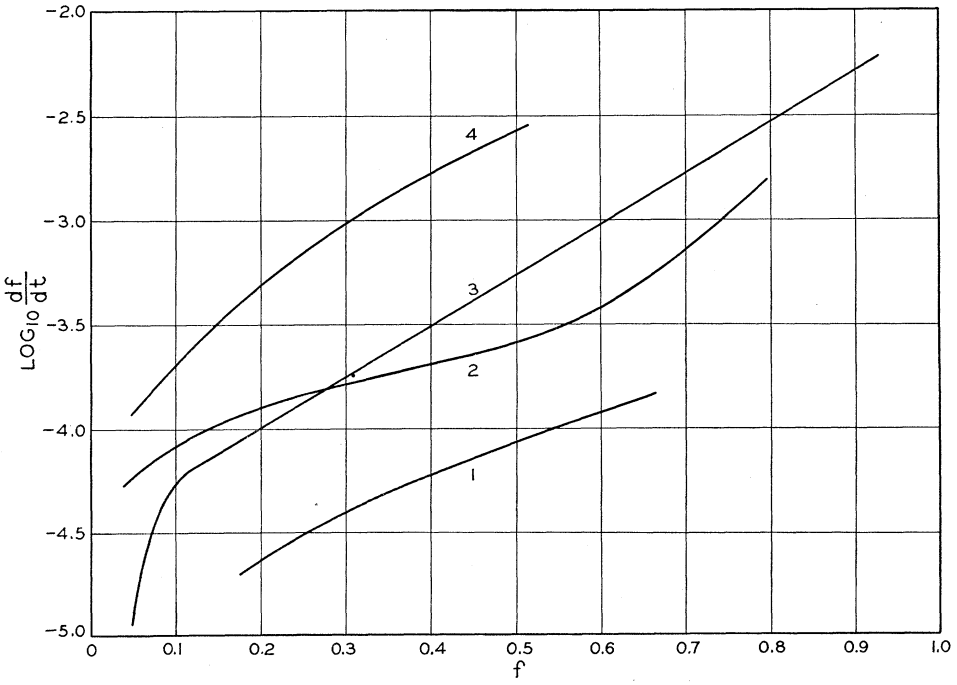

FIG. 17. Comparison of evaporation rates as determined by Andrews (1), Langmuir (2), authors (3) and Eglin (4).

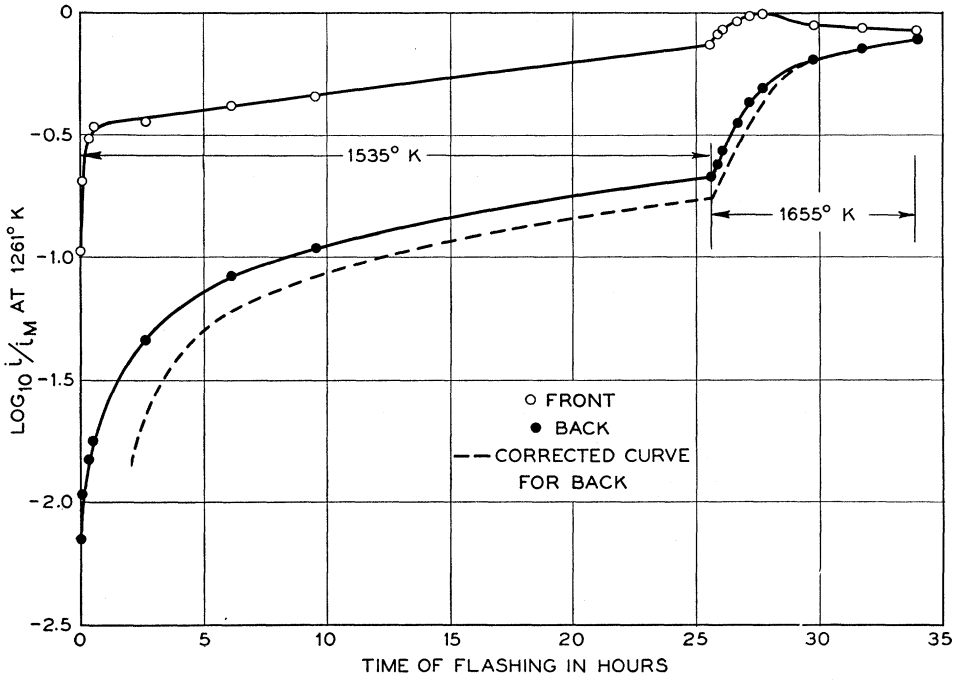

FIG. 18. Changes in activity of front and back of the tungsten ribbon caused by migration of thorium.

each interval of flashing at 1535°K. After 25.5 hours of this treatment the flashing temperature was raised to 1655°K and the procedure continued.

It is to be noticed that log (i/i_m) for the front passes through a maximum and that f for the front goes from $f>1$ to $f<1$. Since about 1 electron in 16 from the front side of the ribbon is eventually collected by the back electrodes, the first few values of log (i/i_m) for the back are too large. This effect of course cancels out when the emission currents from the two sides are nearly equal. Approximate correction can be made for this and the dashed curve in Fig. 18 gives these corrected values.

It is now easy to compare the initial and final values of f. At the end of the run log (i/i_m) for the front was 9.930–10 and for the back 9.894–10. The corresponding values of f are 0.89 and 0.87 and the average value is 0.88, whereas one-half of the initial value of f for the front side is 1.77/2 or 0.885. In other words, the average value of f at the end of the run agrees with the half value of the initial f to within 1 percent. This is probably better agreement than might be expected on consideration of the probable experimental error.

We can learn more about the nature of the migration process by comparing the experimental results for migration with calculated results based on a treatment which is similar to that used in the study of diffusion. Such a treatment leads to the following differential equation

$$\partial f/\partial t=\alpha(\partial^2 f/\partial x^2+\partial^2 f/\partial y^2),$$

in which f is equal to the surface concentration at any point, t is the time, x and y are the distances in two mutually perpendicular directions on the surface, and α is a quantity, analogous to the diffusion coefficient, which we will call the migration coefficient. α is defined as the net number of atoms crossing a line of unit length in unit time per unit concentration gradient across the line. In most problems on diffusion, the diffusion coefficient does not depend on the concentration. Whether α depends on the surface concentration f, is a question that can at present be decided only by experiment. If experiment should show that α is independent of f then it could be concluded that the nature of the forces causing migration are similar to those causing

diffusion. On the other hand if α depends on f, then the forces causing migration must differ from those causing diffusion. We shall, (1) assume that α is independent of f; (2) deduce from this how the emission current from the front side of the ribbon should vary with time of migration; and (3) compare this with the experimental result.

In order to apply the above migration equation to our case[17] we set up a system of coordinate axes and take into account the initial conditions and the boundary conditions. Consider a line parallel to the axis of the ribbon and in the middle of the front side. Call this the front axis. Let x be any distance on the surface of the ribbon measured normal to this line. A point in the middle of the back of the ribbon will have a value of $x=w$ where w is the width of the ribbon. Then if y is measured parallel to the axis of the ribbon, $\partial f/\partial y$ and $\partial^2 f/\partial y^2$ will be zero and we can omit $\partial^2 f/\partial y^2$ in the migration equation. When a migration experiment is performed, the initial conditions are: $f=f_0$ for all values of x between $-w/2$ and $w/2$; $f=0$ for all values of x between $w/2$ and w and between $-w/2$ and $-w$. f_0 is the value of f on the front side of the ribbon when $t=0$. The boundary conditions are that for all values of t, $\partial f/\partial x=0$ at $x=0$ and at $x=w$; this follows from the symmetry of the conditions to the right and left of the front axis. Subject to these conditions the solution of the migration equation is

$$f=\frac{f_0}{2}+\frac{2f_0}{\pi}\sum_{m=1}^{m=\infty}\left(\frac{1}{m}\epsilon^{-m^2\alpha\pi^2 t/w^2}\cos\frac{m\pi x}{w}\sin\frac{m\pi}{2}\right).$$

The indicated series converges rapidly and it is not difficult to compute f for any value of x and t. From such a computation a plot was made of f as a function of x between $x=0$ and $x=w/2$ for a series of values of t, expressed in units of $w^2/\alpha\pi^2$. From the log i *vs.* f curve and the computed f *vs.* x curve, i was determined as a function of x. Then by graphical integration i or log i for the front of the ribbon was determined for various values of t. In order to compare t with the time in the experiment we can assign various values to α. The effect of this is to expand or contract the time scale for the computed curve. α is the only disposable constant in the calculation.

Fig. 19 is a plot of the experimental and calculated results. The constant α was chosen so as to make the calculated and experimental values of log (i/i_m) agree at $t=25.5$ hours. This gave a value of α equal to 1.84×10^{-9} cm^2 per sec. at 1535°K. Beyond $t=25.5$ hrs. the time scale for the calculated values of log (i/i_m) was adjusted by a factor equal to the ratio of the slopes of the experimental curves at $t=25.5$ hrs. The corresponding value of α for this new time scale was 2.44×10^{-8} cm^2 per sec. at 1655°K.

From Fig. 19 it is evident that the experimental values of log (i/i_m) increased faster at first and then slower than the calculated values of log (i/i_m). This holds for the entire test including the latter part at 1655°K. From this it follows that the experimental results cannot be explained by choosing a migration coefficient α dependent on temperature only but that α must also depend on the concentration f. As f decreases, α must decrease. This means that the rate of migration at a given temperature and for a given concentration gradient decreases as the concentration decreases. In the experiment the decrease in α with concentration amounted to at least a factor of 2 or 3.

These results are to be expected if our picture of the migration process is similar to that for evaporation. When evaporation takes place, the number of atoms that have sufficient energy to escape from the surface is very small compared with the number that have energy enough to temporarily rise above the surface. It is very probable that these atoms will not return to the surface at the point they started from especially if there is a component of force acting on the atoms in the direction of decreasing concentration. If this is the mechanism of migration then the ease with which atoms can rise above the surface will greatly affect the rate of migration. We know from the evaporation data that the number of atoms that escape from the surface increases as f increases. Hence the number of atoms which rise above the surface should also increase as f increases, and according to our picture the rate of migration should increase with increase in concentration other things being the same.

[17] We are greatly indebted to Mr. R. W. Sears of these laboratories for the mathematical solution of this problem.

This hypothesis for the mechanism of migration may be unnecessarily detailed or too pictorial. A more general hypothesis can be stated as follows: Ordinarily the adatoms are held in equilibrium positions on the underlying surface. These equilibrium positions are determined by the structure of the underlying surface and by the nature of the adatoms. Between any two neighboring positions a potential hill exists. Let us call the lowest value of this potential hill the work function for migration. If an atom is to go from one equilibrium position to a neighboring one it must first be given sufficient kinetic energy to cross this

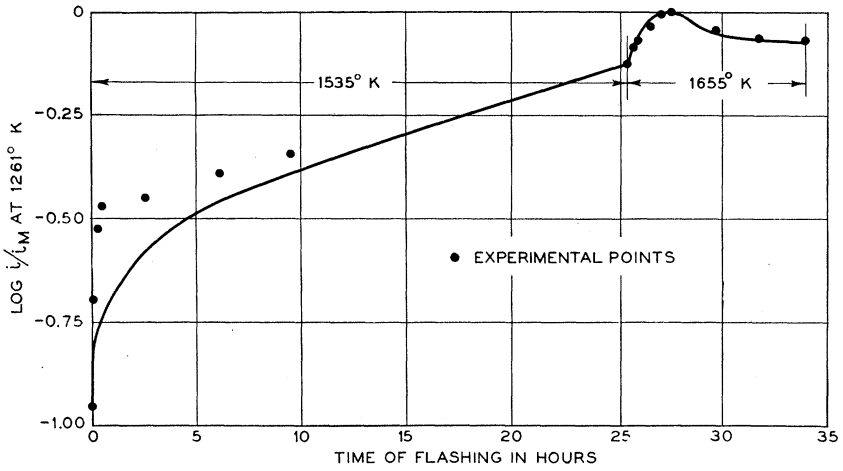

FIG. 19. Comparison of experimental and calculated migration curves for front side of ribbon.

potential hill. This kinetic energy is supplied by thermal agitation and hence the migration rate should increase as the temperature increases.

If the migration work is determined by the nature of the underlying atoms and is not influenced by the concentration of the adatoms, then the rate of migration should be directly proportional to the concentration gradient and should not depend on the concentration. Our experiments show that the migration rate increases with the concentration. Hence it follows that the migration work function must decrease as the concentration increases.

A rough value of the heat of migration can be determined by assuming that an equation of the form

$$\Delta H = 2.3kT^2 (\log \alpha_2/\alpha_1)/(T_2 - T_1) \qquad (21)$$

holds. Where ΔH is the heat of migration and k is Boltzmann's constant. (1.37×10^{-16}.) In the migration experiment, T is roughly 1600°K, $T_2 - T_1$ is 120° and $\log \alpha_2/\alpha_1 = 1.12$. The resulting value of ΔH is 7.5×10^{-12} ergs per particle or 110,000 calories per mol or 4.7 equivalent volts per particle. These values are only approximate and as we have pointed out, they must depend on concentration.

CONCLUSION

In conclusion we wish to emphasize the following points. We have shown that for thorium on tungsten log i is not a linear function of the surface covered as has been assumed in all previous work on thorium on tungsten. The concept of induced evaporation which has been extensively used in the explanation of adsorption phenomena is inapplicable in cases similar to thoriated tungsten. Not only can the activation curves be explained without the use of induced evaporation, but the fact that thorium migrates over the surface at temperatures at which evaporation is negligible shows that an atom which diffuses to the surface at a place occupied by another atom, causes this atom to move along the surface rather than "inducing" it to evapo-

rate. The migration phenomena cannot be explained as a simple process in which the migration rate is directly proportional to the concentration gradient. Finally the data on thermionic and adsorption characteristics of thorium on tungsten presented in this paper are qualitatively the same as in the case of caesium or barium on tungsten. In each of these cases the electron activity passes through an optimum, the evaporation rate at a given temperature varies exponentially with f, and migration takes place more readily than evaporation.