

THE ELECTRON EMISSION FROM THORIATED TUNGSTEN FILAMENTS

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ABSTRACT

Electron emission from tungsten filaments containing thoria.—Ten years ago the erratic behavior of some tungsten filaments was traced to the thoria present and it was discovered that by suitable treatment the filaments, containing 1 to 2 per cent of thoria, could be activated so as to give an electron emission many thousand times that of a pure tungsten filament at the same temperature. Extensive series of experiments have led to the conclusions summarized in this paper. The increased emission is due to a layer of Th atoms adsorbed on the surface of the tungsten. To form this layer, the thorium oxide which originally exists throughout the volume of the filament, must first be reduced in part, by heating for a few seconds to between 2600° and 2800° K; then, by heating for some time at a suitable activating temperature $T_a = 2000^\circ$ to 2100° K, some of the Th atoms are brought to the surface by diffusing faster than they evaporate, the fraction of the surface covered θ , increasing to a limit θ_∞ which may or may not be 1. The activity determined at a lower testing temperature $T_t = 1400^\circ$ to 1500° K, increases logarithmically with θ ; for any filament it remains constant provided the filament is not heated above 1900° K and the film is not allowed to be oxidized. It is evident that the rate of activation $d\theta/dt$ depends directly on the difference between the rate of diffusion to the surface and the rate of evaporation from the surface. *Rate of diffusion of Th atoms to the surface is DG where G is the concentration gradient (atoms per cm^4) of Th atoms near the surface, and D is the coefficient of diffusion. If N_0 is the number of Th atoms per unit area for a saturated film, it seems probable, from the crystal structures of Th and W, that N_0 is only half the number of tungsten atoms in the surface; and making correction for the increased surface due to the dodecahedral structure (6 per cent), N_0 is taken as 0.756×10^{15} . A mathematical analysis of the experimental results gives for the absolute value of D (cm^2 per sec.): $\log_{10} D = .044 - 20540/T$, in agreement with a theoretical expression given by Dushman and Langmuir. *Rate of normal evaporation of Th atoms* from a partly covered tungsten surface ($\theta = .2$ to $.8$) in atoms per cm^2 per sec. is given by: $\log_{10} E_{nm} = 31.43 - 44500/T$. As the surface covered decreases below $.2$, E_n decreases but not as fast as θ , while for values of θ above $.8$, E_n increases to a value three times E_{nm} . The small variation of E_n with θ shows that the effect of adjacent Th atoms is small. Studies of the effect of prolonged activation of filaments indicate that the surface film is never more than one atom thick. Since the atoms do not diffuse back into the tungsten, we must suppose that when a Th atom diffusing to the surface arrives below another Th atom, one Th atom immediately evaporates. *The rate of induced evaporation* depends upon the diffusion and upon θ , experiments showing that $E_i = DG(0.82\theta + .18\theta^2)$. *The rate of activation* is, then, given by: $N_0 d\theta/dt = DG - E_n - E_i = DG(1 - 0.82\theta - .18\theta^2) - E_n$. The experimental curves, however, correspond almost equally well to the simple expression: $d\theta/dt = k(\theta_\infty - \theta)$, when θ_∞ is the limiting value, at which the diffusion and evaporation are balanced. *Deactivation**

occurs when the evaporation exceeds the diffusion. The concentration gradient G depends, of course, on the previous history of the filament, especially the preliminary reduction of thoria at a high temperature. *The rate of reduction of thoria* is given by: $\log_{10} p_r = 27.98 - 30160/T$, where p_r is the number of atoms of thorium produced per sec. per cm^3 ; the limiting concentration gradient (atoms per cm^4) reached is given by: $\log_{10} G_r = 25.22 - 9620/T$, the actual concentrations of thorium in parts per million by weight varying from 1.4 to 200 for temperatures of 1800° to 3000° K. Various properties of thoriated filaments in a steady state are summarized in Table VIII.

Energy changes for atoms of thorium, per gram atom, computed from constants in the above equations are: (1) *Heat of reduction of thoria in tungsten* = $-138,000$ cal. (absorbed); (2) *Heat of evaporation of Th from tungsten* = $204,000$ cal.; (3) *Heat of diffusion of Th through tungsten*: $94,000$ cal.

Crystal structure of tungsten and chromium.—Both are body-centered cubic and when etched show rhombic dodecahedron faces (110). Both show pronounced cubic cleavage (100).

EARLY in 1913 Mr. William Rogers and the writer were endeavoring to determine the electron emission from tungsten filaments in the highest possible vacuum. For this purpose two hairpin shaped filaments were mounted side by side in a tubular bulb. Two platinum wires were sealed through the glass walls on opposite sides of the bulb, the wires being bent so that the part in the bulb lay flush with the inner surface of the glass. After baking out the bulb for several hours at about 400°C and glowing the filaments, the bulb was sealed off, and one of the filaments was then heated for a considerable time at about 2900°K until enough tungsten had evaporated and deposited on the inner surface of the bulb to reduce the resistance measured between the platinum wires to about 100 ohms. Thus a gas free anode was formed and residual gases were removed by the clean-up effect of the vaporized tungsten.

The electron emissions obtained in this way were considerably larger than those previously found under less perfect vacuum conditions. Since earlier work had shown that the clean up is more effective at low bulb temperatures, the bulb was now immersed in liquid air and more tungsten vaporized. With this still better vacuum very great increases in electron emission were obtained, often of many thousand fold. The results even in this vacuum were often erratic and sometimes changed rapidly with time.

It was then found that these increases in emission depended upon the presence of small amounts of thorium in the filament. In making filaments for tungsten lamps it was customary at that time to add a fraction of one per cent of thorium oxide to prevent the occurrence of a phenomenon known as offsetting. Measurements with specially prepared pure tungsten filaments showed that the emission remained unchanged when the bulb was immersed in liquid air, and was, in fact, the same as when

the emission was measured in presence of argon at voltages high enough to ionize the gas. The lower values of the emission from the thoriated filament, obtained for example before the improvement of the vacuum, agreed fairly well with those from the pure tungsten.

During 1913 and 1914 and again especially during the last four years, very detailed studies of the mechanism of the emission from the thoriated filament have been carried out.¹ In the following pages the main conclusions reached in this work will be given, but it will only be possible to give a small fraction of the experimental evidence upon which those are based.

Conditions for obtaining high emission from a thoriated filament. If a thoriated filament is used in place of a pure tungsten filament in ordinary electron tubes, the chances are that nothing unusual will be noted in measuring electron emission, for the thorium on the surface evaporates rapidly at the normal operating temperature of a tungsten filament and is very sensitive to contamination by gases which may oxidize it. The thorium may be protected by using an exceptionally high vacuum such as that obtained by immersing the bulb in liquid air, or by vaporizing into the bulb such substances as sodium, potassium, magnesium or calcium, or traces of vapors of reducing carbon compounds such as hydrocarbons. Magnesium or calcium are most easily introduced by placing small pieces of these metals on the anode or cathode where they may be vaporized during the operation of the tube, or they may be placed on (or in) a small helical tungsten filament mounted in the bulb. Experiments have shown that the emission of a fully activated thoriated filament is the same whether the filament is in a very high vacuum or in sodium or similar vapor.

In the ordinary thoriated tungsten filament nearly all the thorium is present in the form of thorium oxide ThO_2 . Apparently for this reason high emissions are ordinarily not obtained from thoriated filaments until after these have been heated to a very high temperature such as 2600°K or more. A flashing of the filament at 2800°K for 3 minutes is a sufficient preliminary treatment. This probably reduces some of the thorium oxide to metallic thorium which remains distributed at very low concentration throughout the filament. The heating to such a high temperature,

¹ The effect of thorium in increasing the electron emission from tungsten was described by the writer before the American Physical Society on October 31, 1914 (See Phys. Rev. **4**, 544, 1914) but was not published. A full description of the conditions needed to obtain this effect, together with an explanation of the phenomena, was given in U. S. Patents 1244216 and 1244217 issued to the writer on October 23, 1917. Very brief descriptions of some of the observed effects were published in Trans. Amer. Electrochem. Soc. **29**, 137, 1916; Jour. Amer. Chem. Soc. **38**, 2280, 1916, and Phys. Rev. **20**, 107, 1922.

however, removes all thorium from the surface of the filament by evaporation, so that if the temperature is lowered to say 1900°K or less and the emission is measured it is found to be the same as from a pure tungsten filament at the same temperature.

To *activate* the filament metallic thorium must be brought to the surface by diffusion from the interior. This occurs at an appreciable rate only at temperatures above about 1900°K. On the other hand at temperatures above 2200°K thorium evaporates rather rapidly from the surface of the filament. The best temperatures for activating the filament are therefore in the neighborhood of 2000°K or 2100°K.

After the filament has been brought to a very active state by this thermal treatment it will remain indefinitely in this condition if the temperature is kept below about 2100°K, provided the vacuum is sufficiently high or oxidizing gases are eliminated by the presence of easily oxidizable substances such as alkali vapors. In presence of inert gases, etc., the cathode may be deactivated by positive ion bombardment if the positive ions are given high velocities produced for example by high anode voltages.² With lower voltages, the thoriated filament may be kept in an active state in presence of large pressures of argon, alkali vapor, etc., even when the gas is ionized sufficiently to eliminate practically all space charge.

Measurement of the activity of the surface. The activity of the filament under various conditions is studied by measuring the electron emission (saturation current) at some fixed temperature below that at which appreciable diffusion or evaporation occurs. We shall call such a temperature the *testing temperature* and represent it by T_t . If it is desired to study states of activity ranging all the way from pure tungsten to a fully activated surface, a testing temperature of 1500°K is most convenient, for at this temperature the emission from pure tungsten is about 0.1 microampere per cm² while that from the fully activated surface is 18 milliamperes per cm², and this is a good range of current for use with a galvanometer.

The laws governing the activation of a thoriated filament are best determined by means of *activation curves* such as that illustrated by the curve *OAB* in Fig. 1. The typical experimental procedure for obtaining these data is as follows.

Three filaments *a*, *b*, and *c*, each of about 0.0075 cm diameter and 9 cm long, were bent into horseshoe shape and mounted side by side upon a single glass stem by means of platinum leads. This stem was then sealed into a tubular lead glass bulb about 13 cm long and 4.5 cm in

² See K. H. Kingdon and I. Langmuir, Phys. Rev. **20**, 108 (1922)

diameter provided with two flush platinum seals at opposite sides of the bulb near the centers of the filament loops. The glass stem on which the filaments were mounted had an enlargement blown in it between the seal and the flange which by casting a shadow prevented tungsten from depositing on the surface of the flange, thus avoiding leakage currents between the cathode filaments and the tungsten deposit which served as anode.

The bulb was heated several hours to 360°C while being exhausted by a glass condensation pump through a trap immersed in liquid air. During this time the filaments were heated for short times to 2000°K . After cooling the bulb to room temperature the filaments were aged for a few minutes at 2500°K . Each of the filaments was then made anode while charged to $+260$ volts, the other two filaments being heated to 2500°

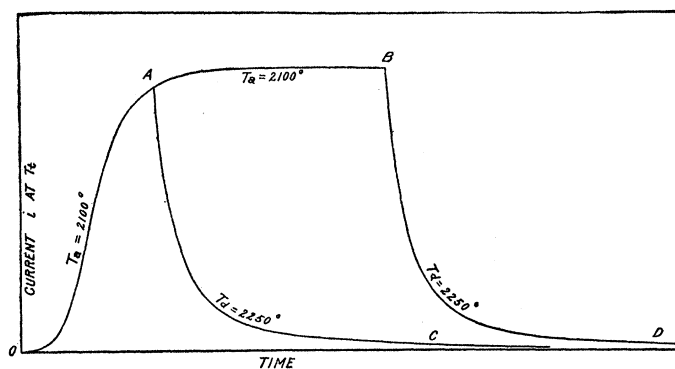


Fig. 1. Rates of activation and deactivation of a thoriated tungsten filament.

and serving as cathode. This treatment heated the platinum leads by electron bombardment. The tube was then sealed off, the bulb was immersed in cold water (or often liquid air) and the central filament (*b*) was heated at 2900° until tungsten had deposited on the walls in such amount that the resistance between the platinum flush seals was only a few hundred ohms. This tungsten deposit, connecting the two platinum seals in parallel, served as anode in all measurements of electron emission from any filament used as cathode, the unused filaments being connected to the negative end of the cathode. For these measurements the anode was kept at 250 volts, this being sufficient to give saturation with the currents used. The bulb was always kept completely immersed in liquid air when the electron emission was measured.

The filament to be studied, which usually contained from 1 to 2 per cent of thorium oxide, was flashed at 2800° for 30 seconds or more, and was then ready for obtaining data for an activation curve. After such

measurements the filament needed to be deactivated before another activation curve could be obtained. For this purpose the filament was heated for a certain time t_d to a *deactivating temperature* T_d at which thorium evaporated more rapidly from the surface than it diffused to it. Temperatures from 2200° to 2600°K were usually chosen as deactivating temperatures.

To determine the rate of activation of the filament at a given temperature the filament was first deactivated and then heated for successive periods of time at the activating temperature T_a . After each of these periods the activity of the filament was determined by measuring the electron emission at the testing temperature T_t . By plotting the electron emission i_t measured at the testing temperature T_t (say 1500°K) as ordinate, against the time t_a during which the filament has been kept at the activating temperature (2100°K) as abscissa, a curve is obtained like that shown by OAB in Fig. 1. The current at first is so small that it cannot be shown in a curve such as Fig. 1 although by using the more sensitive galvanometer shunts the currents are readily measured. After a certain time the curve rises very rapidly about like an exponential function, but then rises more slowly and finally approaches asymptotically a limiting value.

At any given point, such as A in Fig. 1, the activation of the filament may be interrupted and a deactivation curve AC may be obtained by heating the filament for successive short intervals of time at a deactivating temperature T_d which in the case illustrated was 2250°K . After each interval the filament was cooled suddenly by stopping the filament heating current so that the filament would pass rapidly through the range of activating temperatures. The temperature was then raised to the testing temperature and the emission measured.

Nature of the thorium film on activated tungsten filaments. The behavior of thoriated tungsten filaments suggests that the thorium, when it diffuses to the surface, forms an adsorbed film which completely covers the surface. The maximum activity reached by heating at different activating temperatures is the same although the rate of activation may vary greatly. It may seem strange at first that thorium can accumulate in the surface to an apparently high concentration while the concentration in the interior is very small. But this phenomenon is not different from that observed in all solutions containing a solute capable of lowering the surface energy of the solution. For example ether dissolved in water lowers the surface energy and therefore by Gibbs' rule becomes adsorbed in the surface.

The properties of thorium are such that we should expect it to lower the surface energy of tungsten. The Eötvös-Ramsay-Shields relation indicates that the surface energy of any substance at temperatures far below the critical temperature should be proportional to $T_c/V^{2/3}$ where T_c is the critical temperature and V is the atomic volume. Critical temperatures of substances of similar type are proportional to the boiling points at ordinary pressures. Thus for different metals the surface energies should be proportional to $T_b(d/A)^{2/3}$ where T_b is the boiling point, d is the density, and A is the atomic weight. Thorium seems to be about as volatile at 2000°K as tungsten is at 3000°K. The density of thorium is 11.9 while tungsten is 19.4 and the atomic weights are 232 and 184 respectively. Thus each of the three factors differs for the two metals in such a way as to make the surface energy of thorium less than that of tungsten. In fact, from the relation given above, we can calculate that the surface energy of thorium should be only 41 per cent of that of tungsten. Thorium dissolved in tungsten should therefore tend to lower the surface energy and by Gibbs' rule should be adsorbed in the surface.

During the last few years the writer has found evidence of many kinds that adsorbed films do not in general exceed a single atom or molecule in thickness.³ The film of thorium responsible for the high electron emission from an activated filament should also not exceed an atom in thickness. The deactivation curves such as those illustrated in Fig. 1 furnish very direct confirmation of this view. The experiments show that the shape of the deactivation curve is independent of the length of time during which the filament has been allowed to activate. Thus curves *AC* and *BD* in Fig. 1 are identical although the thorium film was allowed to build up for a much longer time in one case than the other. If the film had become thicker than a single atom after the long activation at 2100° there would have been a delay in the falling off of the emission so that the slope of the upper part of *BD* would have been much less than that of *AC*.

There is another indication that the film is never more than one atom thick. If the film of thorium should continue to grow in thickness, we should not expect the increase in emission to follow any simple law, but should find a radical change in the law of increase when the film became more than one atom thick. We shall see, however, that the activation curves such as *OAB* in Fig. 1 are in excellent agreement with simple mathematical equations over the whole range from a fully deactivated condition to that of full activation.

³ A full summary of this evidence with references to the original publications was given in *Trans. Faraday Soc.* **17**, 607 (1921) and reprinted in *Gen. Elec. Rev.* **25**, 445 (1922).

With this conception of an adsorbed film of thorium one atom thick, we can see that the activity of the surface should depend on the fraction of the surface covered by thorium atoms. We shall represent this fraction by θ . We now need to determine the relation between θ and the electron emission i .

It will be shown in a separate paper that the relation between i and θ may be deduced by means of the electric image theory proposed by Schottky.⁵ With the accelerating fields ordinarily used in measuring saturation currents, the electron emission depends upon the number of electrons that have velocity components sufficient to enable them to reach a certain critical surface, about 5×10^{-6} cm out from the cathode surface. At the critical surface the force due to the accelerating field is equal to the attractive force (image force) acting on the electron because of the positive charge which the electron induces in the metallicly conducting cathode surface. The effect of thorium in increasing the emission is not due to a specifically high emission from its surface but results from the positive contact potential of the thorium surface with respect to the tungsten surface. This positive potential of portions of the surface raises the potential at the critical surface and thus increases the number of electrons that can pass this critical region. From this theory it is found that the logarithm of the emission is a linear function of θ so that θ may be calculated from the equation

$$\theta = \frac{\log i - \log i_0}{\log i_1 - \log i_0} \quad (1)$$

where i_0 is the saturation current corresponding to pure tungsten ($\theta=0$) and i_1 is that from the fully activated surface ($\theta=1$) while i is the current when the fraction of the surface covered by thorium has any value represented by θ .

If, for example, the emission from tungsten at a given temperature is one unit while that from a fully activated filament at the same temperature is 100,000 units, then the emission from a surface half covered with thorium ($\theta=0.5$) is not the arithmetic mean of 1 and 100,000 but is the geometric mean 316. Of course if the thorium on the half covered surface should be placed all at one end so that one half the length of the filament was completely covered with thorium while the other half had no thorium the emission would actually be given by the arithmetic mean 50,000. Thus the distribution of the thorium can influence the saturation current.

The electric image theory of the effect, however, indicates directly how uniform the distribution must be in order that Eq. (1) may apply.

⁵ Schottky, *Phys. Zeits.* **15**, 872 (1914)

The thorium influences the emission only by affecting the potential at the critical surface which is at a distance from the surface equivalent to about 200 atomic diameters. Any distribution of thorium which gives a nearly uniform potential at the critical surface will be sufficiently uniform to cause the emission to vary in accord with Eq. (1). Analysis shows that even if the thorium were concentrated into squares like those of a checker-board Eq. (1) would apply fairly accurately if the squares were not larger than about 100 atoms on a side. With any distribution likely to be reached on a plane surface by diffusion or evaporation we should then expect Eq. (1) to apply.

Another relation which follows from the theoretical study of this problem is that the value of b in Richardson's or Dushman's equation for electron emission should also be a linear function of θ so that

$$\theta = (b - b_0) / (b_1 - b_0) \quad (2)$$

where b_0 and b_1 correspond to the values of b for pure tungsten and for a fully activated surface, respectively.

The shape of the activation curve. Whenever the thoriated filament is heated to a high temperature at which deactivation occurs, all thorium evaporates off the surface as fast as it arrives from the interior by diffusion. In the filament just below the surface the concentration gradient should be uniform, when the concentration at the surface is zero. Thorium should thus diffuse to the surface at a practically constant rate during an activation of the filament, except in so far as the supply of thorium in the filament becomes exhausted. Since the amount of thorium needed for activation is only that in a film one atom thick, it seems probable that the available thorium in the filament should suffice for many activations. Experiments show in fact that in a series of activations alternating with deactivations at rather low temperatures where very little thorium is produced by reduction, the rates of activations decrease only very slowly in successive runs. During the early part of any single activation run we should thus expect the thorium in the surface, and therefore θ , to increase at a uniform rate. This means that the logarithm of the current should increase in proportion to the time, or the current should increase exponentially with the time. This is in general accord with the shape of the activation curve shown in Fig. 1, or curve *A* in Fig. 2.

Since the logarithm of the current varies linearly with θ it is more reasonable to plot an activation curve by using $\log i$ as ordinate. Curve *B* in Fig. 2 is plotted in this way from the same data as those used for Curve *A*. The current 0.01 is that from a completely deactivated surface, the dotted line *MN* thus corresponding to $\theta = 0$. The current 1000 is from a fully activated surface, the dotted line *S'R'* corresponding to

$\theta = 1$. Distances measured vertically between these lines MN and $S'R'$ are directly proportional to θ . Thus during the initial part of the activation run, before the current had increased to a value that can be shown on Curve A , the value of θ had risen from 0.0 to about 0.6 and the current had increased about one thousand fold. The fact that the slope of Curve B changes so little in this interval is good confirmation of the linear relation between $\log i$ and θ .

If the thorium diffuses to the surface at a uniform rate and remains in the surface, θ should increase at a constant rate and $\log i$ plotted against t_a should give a curve like MQR' instead of the observed curve B . It is clear therefore that the thorium accumulates at a decreasing rate as θ increases. It was at first thought that such an effect might be due to diffusion from the highly concentrated surface film back into the mass

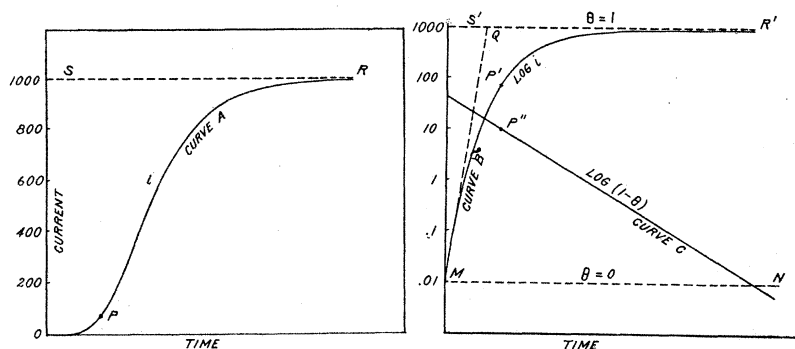


Fig. 2. Rate of activation of thoriated tungsten filaments.

of the filament. It would follow from this that the net rate of arrival of thorium at the surface should fall to zero as the surface film becomes filled ($\theta = 1$); the concentration gradient near the surface would also approach zero, while the concentration itself, just below the thorium film, would increase. The thorium which failed to accumulate in the surface would thus pile up under the surface. It is an easy matter to test whether this is so, for the increased concentration would raise the initial rate of activation in a subsequent run.

Experiments have shown that the thorium does not increase in concentration in this manner after a long activation. In a typical experiment of this kind (Exp. 528, runs M_1 to P_1) the filament was first flashed at 2800° for 23 sec. to get a high thorium content, then heated to 2500° for 100 sec. to allow irregularities in the thorium concentration to become smoothed out. The filament was now run at 2055° for 187 minutes (run M_1). The initial rate of activation (corresponding to the

straight line MQ in Fig. 2) was $d\theta/dt=0.00060$ per sec. while the final rate at the end of the run was less than 0.000003. The filament was now flashed at 2800° for less than one second to distill the thorium from the surface without producing any appreciable fresh supply of thorium. On running the filament again at 2055° (run N_1) the initial rate of activation was 0.00034 showing that the very long previous activation had not caused any accumulation of thorium under the surface but had resulted in a decrease in the thorium concentration.

The filament was kept at 2055° (still run N_1) for a total time of 277 minutes, the activation at this time having come to a standstill (rate less than 10^{-6} per sec.). In order to make sure that the flashing for 1 sec. in the previous run (which had completely deactivated the filament to $\theta=0$) had not vitiated the results by causing a loss of thorium under the surface, the filament was now only partly deactivated by flashing for 3 sec. at 2500° . This flashing lowered the value of θ to 0.78. The filament was brought again to 2055° (run O_1). The rate of activation was now $d\theta/dt=27 \times 10^{-6}$ per sec. whereas in the previous run (N_1) at a similar value of θ the rate had been 61×10^{-6} . If instead of continuing the runs for such great lengths of time, they were stopped after say 30 or 40 minutes, the rates of activation fell off in succeeding runs much less than in the examples shown here. In no case were any indications found of an accumulation of thorium under the surface such as would result from back diffusion from the surface film. We may therefore conclude that under ordinary experimental conditions the formation of the adsorbed film of thorium is an irreversible process in the sense that thorium never goes from the surface back into the body of the filament.

It is clear from these experiments that thorium diffuses continually to the surface of a filament even after the surface film becomes saturated. Since it does not accumulate in the film it must leave the surface in the form of vapor. This is not, however, due to ordinary evaporation of the adsorbed thorium film, for it occurs at a much lower temperature. The phenomenon we have just been discussing (falling off of $d\theta/dt$ with time) is just as well defined at an activating temperature of 1900° as at 2055° but *evaporation* of a completely formed adsorbed film takes place very slowly until temperatures of about 2150° are reached.

Examination of a large number of logarithmic activation curves (like B in Fig. 2) shows that they are accurately represented by an exponential formula of the type:

$$\log(1-\theta) = -kt \quad \text{or} \quad \theta = 1 - e^{-kt} \quad (3)$$

from which we obtain

$$d\theta/dt = k(1-\theta). \quad (4)$$

Let N_0 be the number of thorium atoms per cm^2 in a complete monatomic adsorbed film ($\theta=1$), and let G be the concentration *gradient* just under the adsorbed film, expressed in terms of atoms of thorium per cm^3 per cm ($\text{atoms} \times \text{cm}^{-4}$). If D is the diffusion coefficient (in ordinary c.g.s. units, $\text{cm}^2 \text{sec.}^{-1}$) of thorium through tungsten at the activating temperature, then DG is the rate per unit area at which thorium atoms arrive at the surface by diffusion from the interior. If the surface has just been deactivated ($\theta=0$) no thorium leaves the surface as vapor, but that which first reaches the surface accumulates there. The rate of accumulation of thorium atoms is $N_0 d\theta/dt$ and we may therefore equate this to DG when θ is very small, that is in the range where the curve B (Fig. 2) practically coincides with the straight line MQ . From Eq. (4) we see that $d\theta/dt$ for larger values of θ is proportional to $(1-\theta)$. We may therefore place for all values of θ

$$N_0 d\theta/dt = DG(1-\theta). \quad (5)$$

By comparison with Eq. (4) we see that DG is directly related to k , the rate of activation given by the experiments:

$$DG = N_0 k. \quad (6)$$

From Eq. (5) it appears that the rate at which thorium atoms leave the adsorbed film in the form of vapor is $DG\theta$. It depends not only on the condition of the surface which is defined by θ , but upon the rate at which the thorium diffuses to the surface. We shall therefore refer to this type of vaporization as *induced evaporation* in order to distinguish it from *normal evaporation* which depends only upon the thorium present in the surface film.

The induced evaporation seems to be caused by the difference in the normal rates of evaporation of thorium atoms from tungsten and from thorium. Thus suppose that the normal rate of evaporation of separate thorium atoms in contact only with tungsten atoms is negligible at the activation temperature under consideration, but that the rate of evaporation of thorium atoms which are held by one or more *underlying thorium atoms* is very high compared to the rate of diffusion of thorium to the surface. If a thorium atom diffuses to a point on the surface already covered by thorium, it will cause the evaporation of one of the surface atoms as soon as the incoming atom reaches a position just under the surface atom. The new atom then takes the place of the atom which has just evaporated, but has not contributed anything to the thorium content of the surface. The only case in which the thorium content of the surface does increase is when a thorium atom diffuses to a point in the surface which is not already occupied by thorium. Since the chance that any given place on the surface is unoccupied is $(1-\theta)$ we are led

directly to the conclusion that the rate of growth of the thorium film is proportional to $(1-\theta)$ in agreement with the empirical Eq. (4). We have thus reached a rational derivation of Eq. (5).

If in Fig. 2 we measure distances in arbitrary units from any point P' to the dotted line $S'R'$ and plot the logarithms of these distances as ordinates of a moving point P'' we obtain the line denoted as curve C . Curves B and C are conveniently both plotted on the same sheet of semi-logarithmic paper. If the experimental observations are in accord with Eq. (3) or Eq. (5), curve C will be a straight line whose slope is equal to $2.303 k$, if logarithms to the base 10 are used.

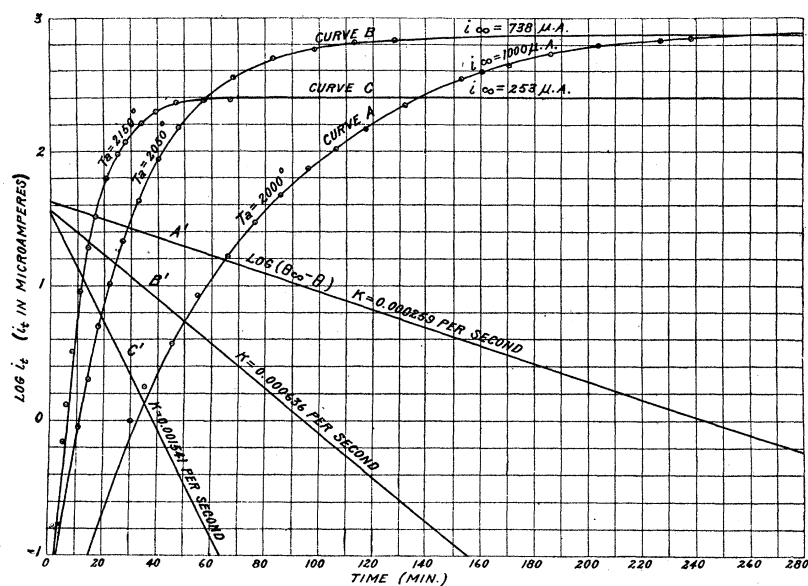


Fig. 3. Rate of activation of a thoriated tungsten filament at temperature T_a after flashing at 2800°K . (Exp. 527, Y, E_1, X_1). Surface of filament = 0.217 cm^2 ; $T_f = 1445^\circ\text{K}$

Fig. 3 is an illustration of typical experimental data. The saturation currents were measured at a testing temperature of 1445°K at intervals during the activation runs. The experimentally determined points are shown by small circles on the logarithmic plots A, B and C . Curve A is a run at an activating temperature of 2000°K . By trial it was found that the limiting value of the current towards which the observed currents were approaching asymptotically was 1000 microamperes. A horizontal line was drawn corresponding to this current and distances were measured vertically in cm from this line to the observed points on Curve A . These were plotted logarithmically (by the method described for curve C ,

Fig. 2) and gave the straight line A' . From this straight line by reversing the above process, the curve shown by the full line marked curve A was calculated. It will thus be noted that curves A , B , and C in Fig. 3 are not merely smooth curves drawn to fit the observations but they are true exponential curves calculated from equations like Eq. (3) by the choice of suitable values of k . It is seen from Fig. 3 that the observed points fall on the calculated curve with high accuracy except for very low values, in the neighborhood of $\log i_t = 0$, which corresponds to currents of about one microampere. Since the currents in this particular set of experiments were measured with a portable microammeter the agreement is still within the error of measurement.

Other experiments made at higher testing temperatures or with more sensitive instruments have shown that the agreement with the exponential equation is, in general, equally good down to the lowest states of activity (where $\theta = 0$). These results not only confirm Eq. (5), but check the accuracy of Eq. (1) and indicate that the whole activation curve follows a single simple law. It is this evidence that was referred to previously in connection with the proof that the thorium film is monatomic.

Evaporation of thorium and deactivation curves. Although the rates of activation could be made to vary widely, even at a given activating temperature, by changing the concentration gradient G , practically the same limiting value of $i_\infty = 1000$, at $T_t = 1445^\circ\text{K}$, was found repeatedly in separate runs at activating temperatures ranging from 1900° to 2100° . But if G had an unusually low value, as for example after heating the filament for many hours at 2300° , the limiting currents found with activating temperatures of 2000° or more were distinctly lower. This effect is due to normal evaporation of thorium from the surface at a rate comparable with the rate of supply of thorium by diffusion from the interior.

Curve C in Fig. 3 at an activation temperature of 2150° illustrates the effect of this evaporation. The rate of activation is much greater than in A , for the rate of diffusion is increased by the higher temperature. But the limiting current i_∞ has fallen to 253 microamp., which corresponds to $\theta_\infty = 0.88$.

If we are to take into account normal evaporation of thorium, Eq. (5) must be modified by subtracting from the second member a term E which we may define as the rate of evaporation expressed in atoms per second per cm^2 of filament surface. The quantity E will depend on the temperature and on θ . The most natural supposition, perhaps, is to assume that E is proportional to θ , viz., the evaporation is proportional

to the amount of thorium on the surface. But we shall see that the experiments indicate that this is not the case. When the surface is very largely covered with thorium it is in fact to be expected that the thorium atoms will tend to hold on to each other and so make the rate of evaporation increase less rapidly than in proportion to θ . Since it is convenient to have an expression for the variation of E with θ let us assume provisionally that E is a linear function of θ . This will always be permissible within a restricted range of values of θ . We may thus place

$$E = \nu_0 + \nu\theta. \quad (7)$$

Subtracting this from the second member of Eq. (5) gives

$$N_0 d\theta/dt = DG(1-\theta) - (\nu_0 + \nu\theta). \quad (8)$$

When $t = \infty$, $d\theta/dt = 0$ and $\theta = \theta_\infty$, so the equation becomes

$$\nu_0 + \nu\theta_\infty = DG(1 - \theta_\infty). \quad (9)$$

Subtracting (9) from (8) and integrating

$$\log \left(\frac{\theta_\infty - \theta}{\theta_\infty - \theta_0} \right) = -kt \quad (10)$$

where θ_0 is the value of θ corresponding to $t=0$ and k is a constant

$$k = (DG + \nu)/N_0. \quad (11)$$

The limiting value of θ is θ_∞ given by

$$\theta_\infty = (DG - \nu_0)/(DG + \nu). \quad (12)$$

The experimental data furnish us with values of k and θ_∞ and from these we wish to find DG , ν_0 and ν . From the above equations we find

$$DG = N_0k - \nu = N_0k\theta_\infty + \nu_0 \quad (13)$$

$$\nu_0 + \nu = N_0k(1 - \theta_\infty). \quad (14)$$

When $\theta_0 = 0$ and $\theta_\infty = 1$, Eq. (10) reduces to Eq. (3). When the rate of evaporation ν is not negligible compared to the rate (DG) at which thorium diffuses to the surface, we see from Eq. (12) that θ_∞ is less than unity, so that the filament does not become fully activated. The linear relation between $\log(1-\theta)$ and t given by Eq. (3), which agreed with experiments where no evaporation occurred, must now be replaced according to Eq. (10) by a linear relation between $\log(\theta_\infty - \theta)$ and t .

Thus in Fig. 3 the lines B' and C' were obtained by plotting as ordinates the logarithms of the vertical distances from points on the curves B or C to the horizontal asymptotes corresponding to the values of i_∞ for the curve in question. It is seen that the agreement between the observed points on curves B and C is as good as it was in the case of curve A . It should be kept in mind that the curves A , B' and C' were *calculated* by means of Eq. (10), choosing of course in each case values of θ_∞ (or i_∞) and k which gave best agreement with the experiments. Activation curves taken under the most varied conditions, even at such high

activating temperatures that θ_∞ did not exceed 0.1, always gave reasonably good agreement with straight lines when plotted in the manner of curves A' , B' and C' .

Run X_1 in Fig. 4, is an example of a *deactivation curve* obtained with the filament at a deactivating temperature T_d of 2300° . Preceding this run the filament had been flashed 30 seconds at 2800° , then run 3 hours

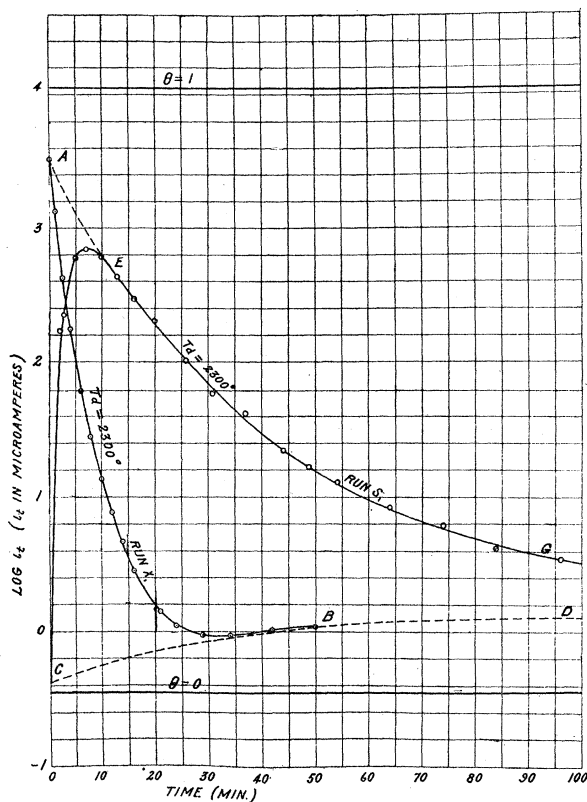


Fig. 4. Deactivation of a thoriated tungsten filament at $T_d = 2300^\circ\text{K}$.
 $T_f = 1630^\circ\text{K}$.

at 2250° and 3 hours at 2100° . This had caused about $4/5$ of the thorium produced at the high temperature to diffuse out of the filament and had thus lowered G to about $1/5$ of its value after flashing. In run X_1 , the activity falls rapidly at first, reaches a minimum and slowly rises to a steady value. This is characteristic of all deactivation curves in which G has previously been brought to a low value.

The reason for the minimum is that the activity depends upon two factors that act in opposite directions; the activity tends to decrease

because of evaporation but the increased production of thorium in the filament due to the higher temperature increases G and tends to raise the activity. Since the latter effect occurs more slowly than the former it is readily seen that the activity should have a minimum.

A second type of deactivation curve, illustrated by run S_1 , Fig. 4, is obtained if the filament is flashed at a high temperature so as to give a high value of G and is then immediately run at a lower temperature. In the case of run S_1 the filament was flashed for 30 seconds at 2800° and then run at 2300° for 106 minutes, the activity being measured at intervals at a testing temperature of 1630° . In this case the activity rises rapidly to a maximum and then falls slowly to the same limiting value (D in Fig. 4) as in the first type of activation curve. There is no minimum activity in this case. The reasons for this shape of curve are similar to those of the first type, but the displacements from the stationary state are in opposite directions. At the beginning of the run there is no thorium on the surface so that evaporation cannot occur, but the thorium arrives at the surface at a rapid rate because of the high value of G . The activity thus increases. In the meantime, however, the thorium is diffusing out of the filament faster than it is being produced so that the value of G steadily but slowly decreases causing finally a decrease in the activity.

In the latter part of both types of curve of Fig. 4 the thorium evaporates from the surface at nearly the same rate as it arrives from the interior so that in a sense a "steady" state may be said to have been reached although this state gradually changes as G increases or decreases. In the first parts of the curves, however, the rates of evaporation and diffusion are not even approximately balanced, the conditions approaching those assumed in the derivation of Eqs. (10) and (11). The steady state corresponds to the case where $\theta = \theta_\infty$ as given by Eq. (12). The dotted curve AE in Fig. 4 is drawn as a continuation of EG and the whole curve AEG corresponds to values of θ_∞ . The sharply rising initial part of run S_1 , marked CE , is thus an activation curve like those illustrated in Fig. 3 except that the value to which the curve approaches (corresponding to θ_∞) is not constant but decreases according to curve AEG . Similarly, CBD represents the limiting current values corresponding to θ_∞ for run X_1 .

From the curves of Fig. 4 we see that the times required for the activity to go 90 per cent of the way to the "steady" value was 4.5 minutes for run S_1 and 19 minutes for run X_1 , these being in a ratio of 1 : 4.2. From Eq. (11) this must also have been the ratio of the corresponding values of $(DG + \nu)$ so that DG in run X_1 must have been at least 4.2 times as great as in run S_1 .

We shall return to a quantitative consideration of activation and deactivation curves after the following section.

Arrangement of tungsten and thorium atoms in surface films. Tungsten crystallizes with a body-centered cubic lattice of atoms, the side of each cube being 3.150 Å.⁶ The shortest distance between atoms (from the center atom to an atom in a corner) is $\sqrt{\left(\frac{3}{4}\right)} \times 3.150$ or 2.728 Å. In a plane (100) through any atom parallel to a face of the elementary cube the number of atoms per cm² is 1.008×10^{15} . In a plane passing through the center atom and any of the edges of the cube (i. e. 110 plane) there are 1.425×10^{15} atoms per cm².

By special heat treatment a square tungsten rod (8×8×100mm) was brought into the form of a single crystal. As it had been held for a long time near its melting point, the surface was distinctly etched by evaporation so that it reflected light in several directions which were not related to the original faces of the rod. By mounting a fragment of this rod on a cork and holding the specimen in a dark room so that the etched crystal faces reflected light from a single lamp placed almost behind the observer's head, it was possible to place pins in the cork indicating the directions of the normals to the crystal faces. Inspection of these pins proved that the faces developed by etching are those of the rhombic dodecahedron (110 planes), all these 12 faces and no others being observed. These are the faces which contain the greatest possible number of atoms. Other single crystals of tungsten were chemically etched by an alkaline ferricyanide solution but only the same faces were found.⁷ Tungsten surfaces which have been heated to such high temperature that some evaporation has occurred, thus consist exclusively of dodecahedral faces. Simple considerations show that the extent of the total developed surface does not increase as the size of the faces increases.

Consider, for example, a single crystal of tungsten having the external form of a sphere, and let this be etched until the original surface is gone and has been replaced by etched dodecahedral faces. Imagine that the sphere be viewed from a point far out along one of the cubic

⁶ Hull, Phys. Rev. **17**, 576 (1921)

⁷ The cleavage surfaces of the single crystal rod were found to be cubic faces (100 planes). Chromium which belongs to the same group in the periodic table, and crystallizes with the body centered cubic lattice, showed pronounced cubic cleavage (100 planes) with a less well developed secondary cleavage along the dodecahedral faces (110 planes). After placing a fragment in dilute hydrochloric acid for a few hours the cubic faces disappeared and the dodecahedral faces were all brought out distinctly. Large crystals of iron, (transformer iron containing a few per cent of silicon) which also showed the body centered lattice, gave on etching in acid only the cubic faces (100 planes).

axes, say the X -axis. From this position only faces parallel to four out of the 12 dodecahedral faces can be seen and each of these faces is inclined at 45° to the line of sight. Every part of the crystal that can be seen must consist of just such faces. Thus if r is the radius of the sphere, the apparent or projected area is πr^2 but the actual area seen is $\sqrt{2} \cdot \pi r^2$.

As this represents only 4 of the 12 faces, the total surface of the etched sphere is $3\sqrt{2} \cdot \pi r^2$ as compared with $4\pi r^2$ for the original sphere. The effect of etching has thus been to increase the surface $3/(2\sqrt{2}) = 1.0607$ fold. The depth of etching has no influence on this ratio as long as the *projected* area of the sphere is not materially changed. The *total surface* of a tungsten filament consisting of small crystals oriented at random is thus 6 per cent greater than its *apparent surface*.

Thorium crystallizes in a face-centered cubic lattice⁸, the side of the cube being 5.04 Å. Since this is a close-packed type of lattice, the thorium atoms behave much like spheres of diameter 3.564 Å. The number of such spheres that can be packed per cm^2 into a plane lattice is 0.909×10^{15} which is only 64 per cent as many as the atoms in the 110 planes in tungsten. We shall see from the data on evaporation of thorium, that forces between adsorbed thorium atoms and the underlying tungsten atoms are very large while those between thorium atoms in adjacent positions on the surface are relatively small. It is therefore highly probable that there is a stoichiometric relation between the number of thorium atoms in a fully active surface and the number of underlying tungsten atoms. A one-to-one relation would involve excessive crowding of the thorium atoms and would be incompatible with small forces between adjacent atoms. We shall therefore assume that there are half as many thorium atoms as underlying tungsten atoms in a fully active surface. Thus the maximum number of thorium atoms in a plane surface is 0.7136×10^{15} per cm^2 . In the case of the surface of an ordinary tungsten filament we must apply the correction due to etching (1.0607) so that the quantity that we have called N_0 in Eqs. (5) to (14) should have the value

$$N_0 = 0.756 \times 10^{15} \text{ atoms per cm}^2. \quad (15)$$

Rate of activation as a function of temperature. At temperatures so low that evaporation of thorium is negligible, the rate of activation, as measured by k , is proportional to the product DG according to Eq. (6). By proper preliminary heat treatment G can be brought to the same value in each of a series of runs carried out at different temperatures. The rate of activation k is then a relative measure of the diffusion coefficient D .

⁸ Hull, Phys. Rev. **18**, 88 (1921)

Table I gives the results of such a series of runs (in the latter part of Exp. 527). Immediately preceding each run the filament was flashed at 2800°K for 5 seconds to bring G to a definite and constant value. The filament temperature was then changed to T_a (Col. 2), this being interrupted at intervals ranging from 5 to 20 minutes for the purpose of measuring the activity at the testing temperature (T_t) of 1445°K. The saturation currents at T_t were plotted on semi-logarithmic paper as illustrated in Fig. 3. The limiting current i_∞ corresponding to $t = \infty$ is given in microamperes in Col. 3. The filament surface from which these currents were obtained was 0.217 cm². By plotting $\log_{10} i_\infty - \log_{10} i$ as ordinate (on the same sheet of semi-logarithmic paper), against time as abscissa, straight lines were obtained as in curves A' , B' , and C' in Fig. 3. The slopes of these lines, after multiplying by 2.303 to convert to natural logarithms and dividing by 60 to convert from rates per minute to rates per second, give directly the values of k defined by Eq. (10). These are tabulated in Col. 4. Col. 5 gives θ_∞ calculated by Eq. (1) from i_∞ of Col. 3 using the values $i_1 = 1300$ and $i_0 = 0.013$ microamperes. Col. 6 gives values of θ_∞ calculated by means of Eq. (14) from data on ν_0 and ν and will be discussed in a later section.

TABLE I

<i>Rates of activation at various temperatures</i>					
Experiment 527	Filament surface 0.217 cm ²				
(1) Run	(2) T_a	(3) i_∞ μ -amps. at $T_t = 1445^\circ\text{K}$	(4) k (10 ⁻⁴ per sec.)	(5) θ_∞ (obs.)	(6) θ_∞ (calc.)
X	2050°K	790	5.31	0.957	0.958
Y	2050	738	6.36	0.951	0.964
Z	2150	253	15.41	0.856	0.856
A_1	2105	477	9.29	0.913	0.913
B_1	2050	707	5.11	0.948	0.957
C_1	2050	805	5.15	0.958	0.957
D_1	1950	1300	1.70	1.000	0.990
E_1	2000	1000	2.59	0.977	0.976

The diffusion of one metal through another must involve interchanges in position between neighboring atoms in the space-lattice. Only atoms containing a certain critical amount of kinetic (or potential?) energy are capable of making such interchanges. The frequency of these changes of position and therefore the diffusion coefficient should thus be proportional to $e^{-Q_D/RT}$, where Q_D may be taken as the "heat of diffusion" or the critical energy (per gram atom) involved in atomic interchanges.⁹ From this relation it appears that the natural logarithm of the diffusion

⁹ S. Dushman and I. Langmuir, Phys. Rev. **20**, 113 (1922)

coefficient is a linear function of the reciprocal of the temperature, the slope of this line being equal to Q_D/R .

To test this conclusion the values of $\log_{10}k$ from Table I have been plotted, in Fig. 5, against $1/T_a$. Since 4 runs were made at $T_a=2050^\circ$, the average was taken of the values of k for these runs, viz. $k=0.000548$. The points lie close to a straight line. Taking $R=1.987$ calories this slope gives $Q_D=94000$ calories per gram atom.

Absolute value of the diffusion coefficient. To determine the actual value of the diffusion coefficient we need to measure some property involving the total thorium content of the filament. Heating the filament momentarily to a very high temperature increases the concentration of

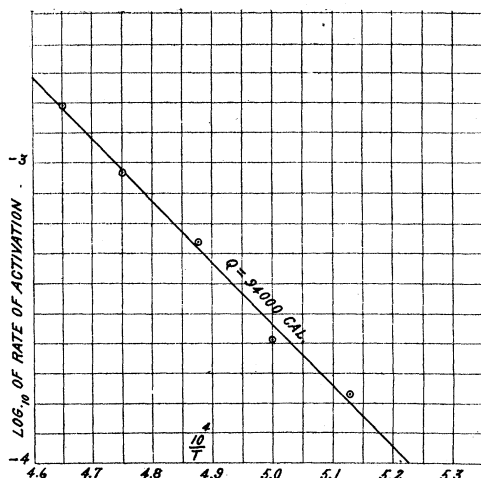


Fig. 5. Rate of activation of thoriated filaments as function of temperature.

thorium. By heating the filament for a long time at a much lower temperature this supply of thorium gradually diffuses out so that the concentration gradient at the surface decreases in proportion. By measuring the product DG from time to time during this exhaustion of the thorium supply, it is possible to determine the absolute value of D .

The diffusion problem involved is analogous to the thermal problem of the cooling of a long cylinder suddenly plunged into a perfectly conducting fluid maintained at a fixed temperature.

This problem has been treated by Carslaw¹⁰ who gives the general equations for the temperature distribution in an infinite cylinder resulting from any initial distribution. For the particular cases required in the

¹⁰ Carslaw, *Fourier's Series and Integrals*, Macmillan and Co., 1906, p. 316

present problem Mr. Harold Mott-Smith has derived the following equations.

Consider an infinitely long circular cylinder in which the concentration (of thorium) is a function $f(r)$ involving only the distance r from the axis of the cylinder. At a certain instant, which we shall choose as origin of time, ($t=0$), the concentration over the whole surface of the cylinder is brought to zero and kept at zero. This is actually accomplished by raising the temperature of the filament suddenly at the time 0 to such temperature that all the substance that diffuses to the surface evaporates immediately. Then after the time t , the *concentration gradient* G at the outer surface of the cylinder is expressible as an infinite series of exponential terms:

$$G = \Sigma B_n e^{-P_n} \quad (16)$$

where

$$P_n = \mu_n^2 D t / R^2 \quad (17)$$

Here R is the radius of the cylinder and D is the diffusion coefficient. The quantities μ_n are the successive roots of the equation $J_0(x) = 0$, where $J_0(x)$ is the zeroth order Bessel function of x . In using the foregoing equations it is merely necessary to substitute the following numerical values of these constants:¹¹

$$\begin{array}{ll} \mu_1^2 = 5.783 & \mu_3^2 = 74.89 \\ \mu_2^2 = 30.47 & \mu_4^2 = 139.04 \end{array} \quad (18)$$

The coefficients B depend upon the initial distribution of the diffusing substance, at the time $t=0$. In case the *concentration* is initially uniform throughout the cylinder and equal to C_u we find

$$B_1 = B_2 = B_3 = \dots = 2C_u / R \quad (19)$$

If the diffusing substance is being produced at a uniform rate throughout the whole body of the cylinder while the concentration at the surface is kept zero, the concentration finally assumes a parabolic distribution given by

$$C = C_p [1 - (r/R)^2] \quad (20)$$

where C_p is the concentration at the axis of the cylinder and C is the concentration at any point whose distance from the axis is r . The concentration gradient G at the surface is then

$$G = 2C_p / R \quad (21)$$

If the production of diffusing substance is suddenly stopped after this parabolic distribution has been reached, as for example by lowering the temperature, the subsequent changes in G are still given by Eq. (16) but the values of the coefficients B now become

$$B_n = 8C_p / (\mu_n^2 R) \quad (22)$$

¹¹ Smithsonian Physical Tables, 1920, p. 68

From Eq. (19) the initial value of G is infinite for the case of initial uniform distribution. With the parabolic distribution, we see from Eqs. (16) and (22) that the initial value of G is $8C_p[\Sigma(1/\mu_n^2)]/R$ which is the same as given by Eq. (21).

From the rapid increase in the exponents (18) in the series (16) it is evident that no matter what the initial distribution may be, the higher terms of the series soon become negligible compared to the first term. Curve II in Fig. 6 is a logarithmic plot of G as a function of time for the

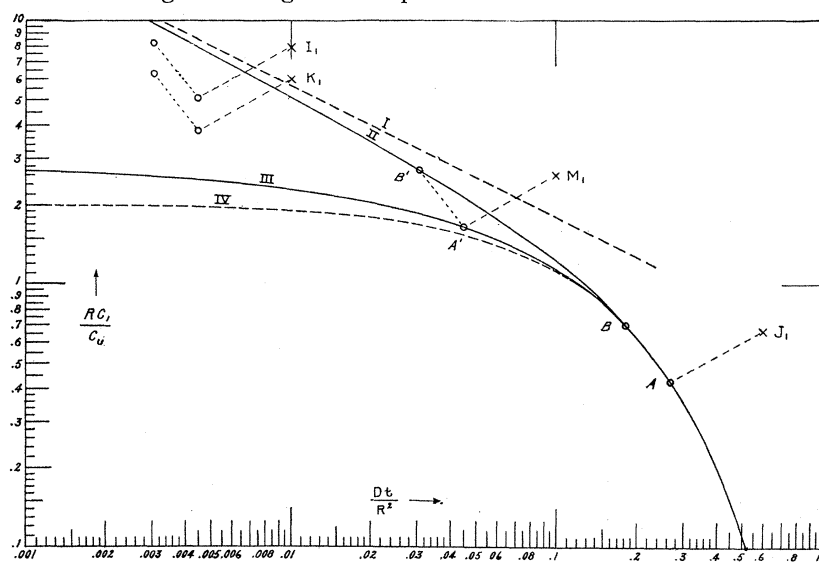


Fig. 6. Transient effects in diffusion in filaments

- Curve I. Initial uniform distribution in semi-infinite solid with plane face.
 Curve II. Initial uniform distribution in cylinder.
 Curve III. Initial parabolic distribution in cylinder.
 Curve IV. First term in series, Eq. (23).

case of initially uniform distribution corresponding to Eqs. (19) and (16). As ordinate, RG/C_u is plotted on the logarithmic scale, while Dt/R^2 is the abscissa on the same scale. This method of plotting has the advantage that any factorial change in R or D or the units in which these or t are expressed, does not change the shape or scale of the curve, but is equivalent to a displacement of the origin of co-ordinates. Curve IV corresponds to the *first term* of the series (16) with the value of B_1 from Eq. (19):

$$G = (2C_u/R)\epsilon^{-at} \quad (23)$$

where by Eqs. (17) and (18)

$$a = 5.783D/R^2 \quad (24)$$

It is seen from Fig. 6 that even when the initial concentration is uniform, G is given with high accuracy by Eq. (23) for all values of t

which make Dt/R^2 greater than about .16. Let us consider on the other hand the case where the diffusion has proceeded for only a short time so that the concentration in the cylinder differs appreciably from the original uniform concentration only in layers whose depth below the surface is small compared to the radius. Then the conditions are essentially similar to those occurring when the plane surface of a semi-infinite solid is suddenly changed in temperature, a problem treated in most books dealing with heat conduction.¹² Thus for the corresponding diffusion problem, when the initial concentration is uniform and the concentration at the surface is brought to zero, we find

$$G = C_u / \sqrt{\pi Dt} \quad (25)$$

To compare this with the functions plotted in Fig. 6 it is conveniently transformed into

$$RG/C_u = 0.564 \sqrt{R^2/(Dt)} \quad (26)$$

which corresponds to the straight line I. For very small values of Dt/R^2 Curve II approaches I but rather slowly.

If the initial distribution is of the parabolic type given by Eq. (20), the concentration gradient G is also expressible, for sufficiently large Dt/R^2 , by the first term of Eq. (16) which now by Eqs. (17), (18), (22) and (24) takes the form

$$G = 1.3833(C_p/R)\epsilon^{-at} \quad (27)$$

By comparing this with Eq. (23) we see that both these functions can be expressed by Curve IV in Fig. 6 if we take

$$C_p = 1.4458C_u \quad (28)$$

In other words the distribution finally becomes the same whether we have initially a uniform concentration or a parabolic distribution with the concentration at the axis 1.446 times as great. Curve III in Fig. 6 gives the values of RG/C_u for this case calculated by means of the *complete* series of Eq. (16) using the coefficients given by Eq. (22). Eq. (27) thus gives a good approximation whenever Dt/R^2 exceeds 0.1.

The total amount q of diffusing substance in the cylinder per unit of length is $\pi R^2 C_u$ when the concentration is uniform. For the parabolic distribution we find from Eq. (20) by integration

$$q_p = \frac{1}{2} \pi R^2 C_p \quad (29)$$

When the distribution has become such that G falls off in accord with Eq. (23) or with Curve IV in Fig. 6, we may find q at any time t from the value of G in Eq. (23) by calculating the total amount of substance that diffuses out to the surface of the cylinder between $t=t$ and $t=\infty$. This gives:

$$q = (4\pi R^2 C_u / \mu_1^2) \epsilon^{-at} = 2.1729 R^2 C_u \epsilon^{-at} \quad (30)$$

¹² See for example Ingersoll and Zobel, Theory of Heat Conduction, p. 77

The distribution within the cylinder under these conditions (i. e., when G is expressible as the first term of the series of Eq. 16) is given by

$$C = 0.8018RGJ_0(\mu_1 r/R) \quad (31)$$

where C is the concentration at any point whose distance from the axis is r . The concentration at the axis is thus equal to $0.8018 RG$.

The absolute value of the diffusion coefficient is most easily found from experiments carried out under conditions such that G varies with time in accord with Eqs. (23) or (27). The experiments on rates of activation of the filament in successive stages thus furnish data for the evaluation of a and from this by Eq. (24) the value of D is calculated.

Several sets of experiments were made to determine D at various temperatures. Most of these were carried out before the complete theory of the diffusion had been worked out, so that the experimental conditions have not always been chosen as well as would otherwise have been possible.

Table II contains data for the calculation of the diffusion coefficient at 2500°K, obtained from Exp. 528. Preceding each of these runs I_1 to M_1 the filament was flashed at 2800°K for 23 seconds in order to bring the thorium content to a definite value. The filament was then maintained at 2500°K for the time given in Col. 2 with the object of causing the concentration gradient G to decrease according to Eq. (16). After the heating at 2500°, the rate of activation k (Col. 4) was measured by running the filament at $T_a = 2055^\circ\text{K}$, interrupting this run at frequent intervals for testing the activity at $T_i = 1450^\circ\text{K}$ in the usual way.

TABLE II

Rates of activation at 2055°K following deactivation at 2500°K for various times
Experiment 528 Filament surface 0.217 cm²

(1) Run	(2) Time at 2500°K (sec.)	(3) i_∞ at 1450°K (μ -amp.)	(4) k at 2055° (per sec.)	(5) θ_∞ from i_∞ (obs.)	(6) θ_∞ (Eq. 42) (calc.)	(7) $k - k_r$ ($\times 10^{-4}$)
I_1	10	760	11.49×10^{-4}	0.976	0.981	7.85
J_1	600	548	4.31	0.947	0.949	0.67
K_1	10	780	9.58	0.978	0.977	5.94
L_1	3660	505	3.64	0.941	0.940	0.00
M_1	100	720	6.22	0.970	0.965	2.58

The values of θ_∞ in Col. 5 were calculated by Eq. (1) from i_∞ in Col. 3 taking $i_0 = 0.01$ and $i_i = 1000$ microamp. The calculated θ_∞ in Col. 6 will be discussed later.

Examination of the data in Col. 4 shows that k decreases rapidly at first and then approaches a limiting value of 3.64×10^{-4} which we shall represent by k_r . In this *stationary state* thorium is being reduced from the

oxide at the same rate as it is lost by diffusion and evaporation. The values of k are proportional to G , so that the equations that we have derived for the variations of G should be directly applicable to our experimental data. Because of the constant production of thorium, however, we use for this purpose not k but $k - k_r$ as given in Col. 7 of Table II. Thus after sufficient time has elapsed for the effect of the higher terms in Eq. (16) to die out, the decay of the quantity $k - k_r$ should follow the exponential law given by Eq. (23). The following method allows us to compare the experimental data directly with the complete Eq. (16) as represented by the curves in Fig. 6.

It is evident that a plot of $\log(k - k_r)$ as a function of $\log t$ should have the same shape and scale as the corresponding curve in Fig. 6 and should differ only by a parallel displacement. The points marked I_1 , K_1 , M_1 , and J_1 are placed in Fig. 6 by plotting $10^4(k - k_r)$ from Col. 7 of Table II against $10^{-3} \cdot t$ where t is the time in seconds from Col. 2. By transferring these points to tracing paper and sliding the paper so as to keep its lower edge horizontal, it is possible to bring any two of the points such as J_1 and M_1 to lie on any desired curve. For example by displacing the tracing paper parallel to the line J_1A the points J_1 and M_1 are brought on to the curve III, which corresponds to the case of parabolic distribution. The points I_1 and K_1 , however, do not fall on this curve but lie between II and III. By displacing the tracing paper by the distance AB the points J_1 and M_1 are brought on to the curve II, corresponding to uniform initial distribution. The points I_1 and K_1 then lie too low. It appears from this that the distribution of thorium is intermediate between the two cases considered. It is more likely, however, that the true distribution resulting from the production of thorium by heating the filament to high temperature approaches closely to the parabolic case if sufficient time is allowed for a stationary state to be reached. It is rather doubtful if the 23 seconds allowed in these experiments was long enough. Failure to reach the stationary state would cause deviations of the type observed.

By having placed the observed points on the theoretical curve in this manner, we determine the absolute value of Dt/R^2 , and from this since t and R are known, we find D . Thus if we assume initial parabolic distribution we find Dt/R^2 for the point A to be 0.27. For this point $t = 600$ sec., and therefore since $R = 0.00389$ cm we find $D = 6.8 \times 10^{-9}$ cm² per second for 2500°K. Similarly if we assume initially uniform distribution, Dt/R^2 for point B is found to be 0.18 which gives $D = 4.3 \times 10^{-9}$ cm²/sec. Of course the same values for D are found from the other pairs of points.

The diffusion coefficient at 2055°K was determined by a series of prolonged activation runs, N_1 , O_1 , and P_1 carried out at this temperature. Just preceding run N_1 the filament was flashed for a couple of seconds at 2800°K. In run N_1 the filament was maintained at 2055° for 277 minutes, the activity being tested at frequent intervals in the usual way. The filament was then flashed at 2500° for 3 seconds, a time so short that the filament was only partly deactivated and G was not altered. Run O_1 then followed, the filament being kept at 2055° for 110 minutes. After flashing for 4 seconds at 2500° an activation curve was again made (run P_1) at 2055°. Selecting from these runs points corresponding to a definite value of θ we obtain the following data¹³

Run	t	k	$k - k_r$
N_1	30 min.	3.59×10^{-4}	3.06×10^{-4}
O_1	305	1.62	1.09
P_1	475	1.25	0.72

Plotting these on tracing paper and comparing with the Curve III of Fig. 6 the most probable value of the diffusion coefficient at 2055° is found to be 1.1×10^{-10} cm² sec.⁻¹.

The deactivation curve of run S_1 shown in Fig. 4 furnishes excellent data for the calculation of D at 2300°. We have seen that the portion EG of the curve CEG results from the gradual decrease in G as the supply of thorium becomes exhausted. In the region represented by CE the rate of change of activity is so great that the term $N_0 d\theta/dt$ in Eq. (8) is at least comparable in magnitude with the terms in the second member of the equation. In the region EG , however, $d\theta/dt$ has become so small that the corresponding term may be neglected in comparison with those in the second member. Eq. (8) thus becomes

$$DG = (\nu_0 + \nu\theta)/(1 - \theta) \quad (32)$$

The quantity G given by this equation cannot be used directly to determine the diffusion coefficient according to Eq. (16), for the constant production of thorium at 2300° must be allowed for. Let G_r be the limiting value of G which would be reached when the accumulated surplus of thorium has been exhausted, the rate of loss of thorium by diffusion being then equal to the rate of production. The value of G_r can be expressed in terms of θ_r , the corresponding value of θ , by an equation similar to Eq. (32). We now substitute in the diffusion equations the quantity $(G - G_r)$ just as we previously used $(k - k_r)$. Eq. (32) gives

$$\frac{D}{\nu + \nu_0} (G - G_r) = \frac{1}{1 - \theta} - \frac{1}{1 - \theta_r} \quad (33)$$

¹³ The value of k_r was taken to be 0.53×10^{-4} as calculated from values of G_r which will be discussed later.

The quantities in the second member are both easily found from the experiments. Taking the logarithm of the second member and plotting against the logarithm of the time as in Fig. 6, the absolute value of D is found. The data of run S_1 in Fig. 4, are in complete agreement with the curves of Fig. 6, in the range beyond $t=40$ minutes corresponding to the region where the curves II, III and IV coincide. For smaller values of t , the experimental curve lies somewhat above Curve II. This should not be taken as evidence, however, that there is a uniform rather than a parabolic distribution of thorium in the filament for it is probable that the deviations from the Curve III are due to variations of the rate of evaporation as a function of θ , from the linear relation assumed in Eq. (7) upon which Eq. (33) is based. The assumption of this linear relation is always justifiable over a narrow range of values of θ , but becomes open to question when applied to the wide range covered by the data of run S_1 .

If we therefore confine our attention to the portion of run S_1 taken after the first 40 minutes we find by our comparison with Fig. 6 the value $D=1.12 \times 10^{-9}$ cm² sec⁻¹. Since in this region the effects of the uncertain initial distribution of thorium are eliminated, so that only the first term in the series of Eq. (16) need be considered, a simpler method may be employed. Plotting the \log_{10} of the second member of Eq. (33) against the time t (on semi-logarithmic paper), a straight line is obtained. The slope of this line, multiplied by 2.303, gives directly the value of α defined by Eq. (24). From this the value of D is found, and is of course the same as that obtained by the curves of Fig. 6.

Run T_1 was made to determine the diffusion coefficient at 2400°. The filament was first flashed at 2800° for 30 seconds and then run at 2400° for deactivation, the activity being measured at a testing temperature of 1800°. The run was interrupted three times for the purpose of determining the value DG/N_0 by means of very short activation runs of 5 to 10 minutes at 2100°. The values of θ and $d\theta/dt$ were found in these runs from which, by Eq. (8), DG/N_0 could be calculated, the term $(\nu_0 + \nu\theta)$ being applied as a small correction determined from data which will be discussed later. The results obtained from run T_1 are

t (minutes at 2400°K)	DG/N_0 (at 2100°K)	$D(G-G_r)/N_0$ (at 2100°K)
4.7	7.67×10^{-4} sec. ⁻¹	3.86×10^{-4} sec. ⁻¹
23.1	4.65	0.84
45.6	3.95	0.13

All three of the observations recorded in this table, when compared with the curves of Fig. 6, are found to lie in the region where the Curves II, III and IV coincide. It was therefore assumed that the exponential type of equation such as (23) is applicable. The value of G_r was found by trial so as to make the three points corresponding to the data in the third column give a straight line when plotted on semi-logarithmic paper against the time t . The slope of this line gave $\alpha = 0.00140 \text{ sec.}^{-1}$, from which Eq. (24) gives $D = 3.57 \times 10^{-9} \text{ cm}^2 \text{ sec.}^{-1}$ at 2400°K .

Table III contains a summary of the absolute values of the diffusion coefficient obtained in the way just described. The logarithms of these values of D are plotted against the reciprocals of the temperatures in Fig. 7. The straight line marked D has been drawn to have the same slope as the line in Fig. 5, which corresponds to a heat of diffusion of 94000 calories per g-atom. The agreement with the observed points is very satisfactory, especially when it is considered that several different methods have been used in determining the relative and the absolute values of D .

TABLE III

Experimentally determined values of the diffusion coefficient of thorium through tungsten

Run	Temperature	Diffusion coefficient D ($\text{cm}^2 \text{ sec.}^{-1}$)
N_1 to P_1	2055°K	1.1×10^{-10}
S_1	2300	1.12×10^{-9}
T_1	2400	3.57×10^{-9}
I_1 to M_1	2500	6.8×10^{-9}

The straight line in Fig. 7 gives the following equation for the diffusion coefficient at any temperature (in $\text{cm}^2 \text{ sec.}^{-1}$):

$$\log_{10} D = 0.044 - 20540/T \quad (34)$$

Table IV gives values of D calculated by this equation.

Rate of production of metallic thorium. The data furnished by low temperature activation curves enable us by Eq. (6) to calculate DG and now that we know the values of D from Table IV we can obtain the value of G . We have seen from Table II that after the filament had been heated a long time at 2500° , k_r (at 2055°) approached a limiting value of 0.000364. From the value $D = 1.12 \times 10^{-10}$ and by Eqs. (6) and (15) we thus find $G_r = 2.46 \times 10^{21}$ atoms of thorium per cm^4 at 2500° . In a similar way from data of about 20 other sets of activation runs, values of G_r for temperatures ranging from 2055° to 3000° have been

obtained. The logarithms of these values plotted against the reciprocals of the temperatures give a straight line whose equation is

$$\log_{10} G_r = 25.22 - 9620/T. \quad (35)$$

The slope of this line multiplied by 4.575 gives $Q = 44000$ calories per g-atom. Let p_r be the rate of production of thorium per unit volume throughout the filament. When the steady state has been reached in which the concentration gradient at the surface is G_r , the rate of production of thorium per unit length is $2\pi RDC_r$, and thus

$$p_r = 2DG_r/R \quad (36)$$

TABLE IV

Diffusion coefficient of thorium in tungsten and the rate of evaporation of thorium adsorbed on tungsten

T	D ($\text{cm}^2 \text{ sec.}^{-1}$)	E (atoms per $\text{cm}^2 \text{ sec.}$)	T	D ($\text{cm}^2 \text{ sec.}^{-1}$)	E (atoms per $\text{cm}^2 \text{ sec.}$)
1400°K	2.36×10^{-16}	0.445	2200°K	5.10×10^{-10}	1.61×10^{11}
1500	2.24×10^{-14}	58.5	2300	1.30×10^{-9}	1.22×10^{12}
1600	1.61×10^{-13}	4.18×10^3	2400	3.06×10^{-9}	7.80×10^{12}
1700	9.15×10^{-13}	1.81×10^5	2500	6.73×10^{-9}	4.31×10^{13}
1800	4.29×10^{-12}	5.15×10^6	2600	1.39×10^{-8}	2.08×10^{14}
1900	1.71×10^{-11}	1.03×10^8	2800	5.11×10^{-8}	3.48×10^{15}
2000	5.94×10^{-11}	1.53×10^9	3000	1.58×10^{-7}	3.99×10^{16}
2100	1.83×10^{-10}	1.75×10^{10}			

The temperature coefficient of p_r is thus the sum of those of D and G_r . Substituting into Eq. (36) the values of D from Eq. (34), G_r from Eq. (35) and $R = 0.00389$ cm, we obtain

$$\log_{10} p_r = 27.98 - 30160/T, \quad (37)$$

p_r being expressed in atoms of thorium per sec. cm^3 . The heat of the reaction involved in the production of the thorium is thus $Q_r = -138000$ calories per g-atom, the negative sign indicating that the reaction involves the absorption of energy.

Although in Exps. 527 and 528 the filaments were heated for several hours per day for more than 3 months there was no indication of a falling off in the rate of production of thorium. Because of the induced evaporation, all the thorium produced at the rate p_r leaves the filament even at relatively low temperatures. The data used in calculating p_r in Eq. (37) were obtained with a filament containing 1.0 per cent of thorium oxide, corresponding to 4.4×10^{20} atoms of thorium per cm^3 . If the thorium were produced at a constant rate p_r the life of the thoria would be $4.4 \times 10^{20}/p_r$ seconds or $1.22 \times 10^{17}/p_r$ hours. In this way we calculate that the thoria supply should last 94000 hours at 1900°. Col. 5

of Table VIII contains data on the life at different temperatures. Considering that the rate of production of thorium must decrease as the thoria content falls off, the "life" calculated in this way probably represents the time required for the thoria to fall to one eth of its initial value. For different filaments, even containing the same amount of thoria, p_r varies considerably depending on the mechanical state of subdivision of the thoria in the filament and on other factors. The presence of even traces of carbon tends to reduce the thoria to thorium and greatly increases p_r . Filaments containing different amounts of thoria but otherwise alike seem in general to give values of p_r proportional to the amount of thoria.

Amounts of thorium metal present in the filaments. We see from Eq. (29) in the case of parabolic distribution, that the average concentration throughout the filament is one-half that at the center and thus according to Eq. (21) it is equal to $GR/4$. In the stationary state we may replace G by G_r which we find from Eq. (35), and thus taking $R=0.00389$ cm and by converting from atoms per cm^3 to parts by weight by dividing by 5.0×10^{22} we obtain the following average concentrations of metallic thorium in parts per million.

1800°	1900°	2000°	2100°	2200°	2400°	2800°	3000°K
1.4	2.8	5.0	8.4	14	32	118	200

Relation between induced evaporation and θ . The activation curves obtained in Exp. 528 after the filament had been well aged gave straight lines when $\theta_\infty - \theta$ was plotted on semi-logarithmic paper against the time, i.e., the data agreed with Eq. (10) which was derived on the assumption that G is constant. The foregoing analysis, however, indicates that in the neighborhood of 2100°, G should change considerably during the run if G is initially very different from the stationary value G_r .

For example in an activation run at 2100° (first part of run U_1) which followed after a flashing at 2800° for 30 seconds, θ increased from 0.01 to 0.83 in 20 minutes. The line obtained by plotting $\theta_\infty - \theta$ on semi-logarithmic paper was so nearly straight that its slope did not change more than 2 per cent in the course of its length, while calculation by Eq. (23) shows that G should have decreased about 6 per cent. Run N_1 furnishes a more striking example for the slope remained constant during the whole run of 277 minutes at 2055° although G decreased 55 per cent during this time.

This result may be explained by assuming either that θ is not strictly a linear function of $\log i$, or that the induced evaporation is not quite proportional to θ . Taking the latter assumption as the more probable, it has been found that the data of runs U_1 and N_1 , as well as several

others of a similar nature, are very satisfactorily accounted for if the factor $(1-\theta)$ in Eq. (8) is replaced by

$$f(\theta) = 1 - 0.82\theta - 0.18\theta^3, \quad (38)$$

the last 2 terms representing the induced evaporation.

Thus when θ is small, the chance is 0.82θ that an atom of thorium in arriving at the surface shall cause the evaporation of one already on the surface. But when θ is nearly unity, the chance that an atom of thorium arriving at the surface can find a place in the surface without driving off one already present is $1.36(1-\theta)$. This suggests that the thorium atoms are not closely packed in the surface film even when $\theta=1$.

Normal evaporation of thorium. The actual rate of evaporation of thorium may now be calculated from the experimental data by Eq. (8). For the present, however, we do not need to assume that this rate is a linear function of θ and will therefore write the equation in the form

$$N_0 d\theta/dt = DG f(\theta) - E, \quad (39)$$

where $f(\theta)$ is given by Eq. (38) but with sufficient accuracy for most purposes may be placed equal to $(1-\theta)$.

As an illustration of the method used in calculating the values of E as a function of θ , let us consider the data of run X_1 given in Table V.

TABLE V
Rate of evaporation of thorium as a function of θ
Data from Run X_1 , Exp. 528
 $D = 1.30 \times 10^{-9}$ $G_r = 1.09 \times 10^{21}$ Filament temperature 2300°K
 $R = 0.00389$ cm

(1) t_m (min.)	(2) θ	(3) $10^4 d\theta/dt$ (per sec.)	(4) $f(\theta)$	(5) $10^{-11} DG$ (atoms cm^{-2} sec. ⁻¹)	(6) $10^{-11} E$ (atoms cm^{-2} sec. ⁻¹)
0	0.883	-15.95	0.152	7.86	13.25
2	0.721	-11.73	0.341	9.07	11.96
4	0.599	-9.14	0.472	9.60	11.44
6	0.500	-7.39	0.567	9.98	11.24
8	0.419	-6.13	0.640	10.36	11.26
10	0.352	-5.11	0.702	10.58	11.29
12	0.296	-4.20	0.752	10.81	11.30
16	0.201	-3.35	0.833	11.26	11.91
20	0.141	-1.72	0.885	11.64	11.60
24	0.111	-1.01	0.909	11.94	11.62
28	0.094	-0.44	0.925	12.25	11.33

The values of θ were calculated by Eq. (1) from the saturation currents i shown in Fig. 4. The derivative $d\theta/dt$ was obtained much more accurately than would be possible from a direct plot such as Fig. 4, by plotting $(\theta - \theta_\infty)$ on semi-logarithmic paper against t so as to obtain a curve which

was very nearly straight, whose slope could thus be accurately measured at any point. According to Eq. (10) this slope is equal to k which is here considered variable and it is evident that

$$d\theta/dt = -k(\theta - \theta_\infty) \quad (40)$$

The value of the derivative found in this way is independent of the choice of θ_∞ .

The values of DG in Col. 5 are calculated by means of Curve III in Fig. 6, in the following manner. In run V_1 the filament had been heated for several hours at 2250° until G had reached its stationary value G_r which by Eq. (35) is equal to 8.8×10^{20} at 2250° . In run W_1 which followed immediately after V_1 , the filament was at 2105° for 196 minutes during which G fell from 8.8×10^{20} to 6.2×10^{20} while θ rose from 0.12 to 0.857. The filament was then maintained at 2000° for 47 minutes which lowered G to 6.05×10^{20} and raised θ to 0.883, and this was the condition of the filament at the beginning of run X_1 which followed. The initial value of DG at the head of Col. 5 (Table V) was obtained by multiplying G by 1.30×10^{-9} , which is the value of D at 2300° from Table IV.

From t_m , the time in minutes in Col. 1, we obtain Dt/R^2 and from Curve III in Fig. 6 find the corresponding values of RG/C_u . These are proportional to $DG - DG_r$, and thus, since we know the initial value of DG and obtain $G_r = 1.09 \times 10^{21}$ at 2300° from Eq. (35), we calculate the remaining values of DG in Col. 5.

The rates of evaporation E given in the last column are calculated by Eq. (39) from the corresponding values of $d\theta/dt$, DG and $f(\theta)$ in columns 3, 5 and 4; N_0 being given by Eq. (15). Although θ decreases in the ratio 10 to 1, E decreases by only 15 per cent, and over most of the range may be taken as constant.

In run S_1 , which is also shown in Fig. 4, a similar analysis indicates that DG at $t=5$ minutes, was 52×10^{11} and fell to 15×10^{11} at $t=106$. Notwithstanding these much higher values of DG , the values of E were not essentially different, averaging 16.3×10^{11} in the range $\theta=0.7$ to 0.2 while a similar average in run X_1 gives 11.5×10^{11} . This difference is equivalent to a change in temperature of 18° at 2300° . In run S_1 also, E was practically independent of θ .

The evaporation data from run X_1 are probably much more reliable than those from run S_1 , since in the former run the term containing DG in Eq. (39) was much smaller in comparison with the $d\theta/dt$ term than in the latter run. The ratios of the values of these terms at the beginnings of these runs were 1:10 and 4.5:1 respectively. Of course the factor DG during the course of a run is subject to considerable uncertainty as it is not determined directly but is calculated

from the data of Fig. 6 and involves assumptions as to the distribution of thorium throughout the filament. The term involving $d\theta/dt$ on the other hand is found from the experimental data. Therefore it is felt that very little weight should be given to determinations of E in runs such as S_1 in which G had high values.

Two other methods were used in some experiments to determine values of E . These may be illustrated by the data of run V_1 . The filament was first heated at 2800° for 30 seconds, and then run at 2195° for 60 minutes, at which time the temperature was changed to 2250° . Between the first and the 12th minute at 2195° , θ increased from 0.23 to 0.88, and the values of $(\theta - \theta_\infty)$ gave on semi-logarithmic paper a straight line whose slope corresponded to $k = 35.5 \times 10^{-4} \text{ sec.}^{-1}$. The value of θ_∞ which had to be chosen to get this straight line was 0.943. Substituting these values in Eq. (14) gives $\nu_0 + \nu = 1.53 \times 10^{11}$. Assuming, in accord with the result of run X_1 that $\nu = 0$ in comparison with ν_0 , Eq. (13) becomes $DG = N_0 k$, which gives $DG = 26.8 \times 10^{11}$, or taking $D = 4.85 \times 10^{-10}$ at 2195° by Eq. (34) we find $G = 5.53 \times 10^{21}$, and $E = 1.53 \times 10^{11}$.

During the remainder of the run at 2195° , θ increased to a maximum of 0.921 at $t = 24$ minutes and then decreased slowly as in run S_1 , Fig. 4. At $t = 60$ min. the data showed $\theta = 0.882$ and $d\theta/dt = -0.20 \times 10^{-4} \text{ sec.}^{-1}$, the filament temperature still being 2195° . When at this point the temperature was changed to 2250° the filament was rapidly deactivated, so that the curve of θ as a function of t gave a sharp kink, the slope changing abruptly from -0.20×10^{-4} to -4.5×10^{-4} . Substituting these data obtained just before (1) and just after (2) the change of temperature into Eq. (39) together with the value of N_0 from Eq. (15) we get the equations,

$$-0.15 \times 10^{11} = D_1 G f(\theta) - E_1$$

$$\text{and} \quad -3.40 \times 10^{11} = D_2 G f(\theta) - E_2$$

where $D_1 = 4.85 \times 10^{-10}$, and $D_2 = 8.22 \times 10^{-10}$, and $f(\theta) = 0.153$ (for $\theta = 0.882$). Solving these equations we find

$$G = 1.35 \times 10^{10} E_1 - 0.20 \times 10^{21}$$

$$\text{and} \quad E_2 = 3.15 \times 10^{11} + 1.69 E_1$$

In this way by measuring the change in slope caused by a change in temperature, the value of E at one temperature can be found from that at another. If in this example we take the value $E_1 = 1.53 \times 10^{11}$ found from the first part of run V_1 we obtain $E_2 = 5.74 \times 10^{11}$ as the rate of evaporation at 2250° and $G = 1.86 \times 10^{21}$ which is about one third the concentration gradient found at the beginning of the run.

Table VI contains a summary of the most reliable data on the rate of evaporation in Exp. 528. Col. 2 indicates the method used to determine

E , the three methods which have been described above being designated respectively I, II and III. The letter A or D is used to indicate whether the filament became activated or deactivated during the run. Col. 4 describes the condition into which the filament has been brought by its previous treatment; it gives the value of G observed in the middle of the range of θ covered by the run. In some of the runs θ varied over a wider range than indicated in Col. 5, but the value of E given in the last column is based on the observations in the range given and in this range E seemed to be substantially independent of θ .

TABLE VI
Summary of data on rate of evaporation of thorium. Experiment 528

Run	Method	Temp.	$10^{-21}G$	Range of θ	E
N_1	I-A	2055°K	1.9	0.4-0.8	6.2×10^9
W_1	II-A	2105	0.75	0.2-0.8	1.98×10^{10}
Q_1	I-D	2150	0.61	0.82	5.5×10^{10}
Q_1	I-D	2195	0.57	0.7-0.4	1.7×10^{11}
V_1	II-A	2195	5.5	0.2-0.9	1.53×10^{11}
V_1	III-D	2250	1.9	0.88	5.74×10^{11}
R_1	I-D	2300	0.54	0.38	1.3×10^{12}
X_1	I-D	2300	0.81	0.7-0.2	1.15×10^{12}
G_1	I-D	2400	1.7	0.6-0.4	8.8×10^{12}
U_1	I-D	2450	4.6	0.8-0.3	1.60×10^{13}

In Fig. 7 the logarithms of E are plotted against the reciprocal of the temperature. It is seen that the points lie along a straight line which corresponds to¹⁴

$$\log_{10} E = 31.434 - 44500/T. \quad (41)$$

Values of E calculated from this equation at intervals of 100° are given in Table IV. The slope of the line in Fig. 7 is 44500 degrees which corresponds to a heat of evaporation of 204000 calories per g-atom.

Although in the range of θ covered by the foregoing runs, E is found to be nearly constant at any given temperature it is certain from kinetic considerations that E must become proportional to θ for sufficiently small values of θ where each thorium atom must act independently of others. In fact a few runs which had been carried to particularly low values of θ gave some indication of a falling off in E . In run U_1 at 2450° E was practically constant between 0.2 and 0.8 but at $\theta=0.1$ had fallen to 65 per cent and at $\theta=0.07$ to 48 per cent of its value at $\theta=0.2$.

¹⁴ In the abstract in the Phys. Rev. 20, 107 (1922), the first term in the second member of this equation was given as 7.76. In the early work ν was used to express evaporation in terms of *gram atoms* $\times \text{cm}^{-2} \text{sec}^{-1}$. In the abstract the definition of ν was given in atoms instead of gram atoms but by an oversight the equation was not correspondingly altered by multiplying by the Avogadro constant 6.1×10^{23} .

To get more information as to the evaporation in this region of low θ about 30 runs were carried out in Exp. 528 (after run X_1) with values of θ ranging from 0.02 to 0.3. The data were very consistent but in view of more recent experience with other types of active cathodes, it seems probable that they were subject to considerable errors due to incomplete evaporation of thorium from portions of the filament near the leads which were at a somewhat lower temperature. It is evident, because of the

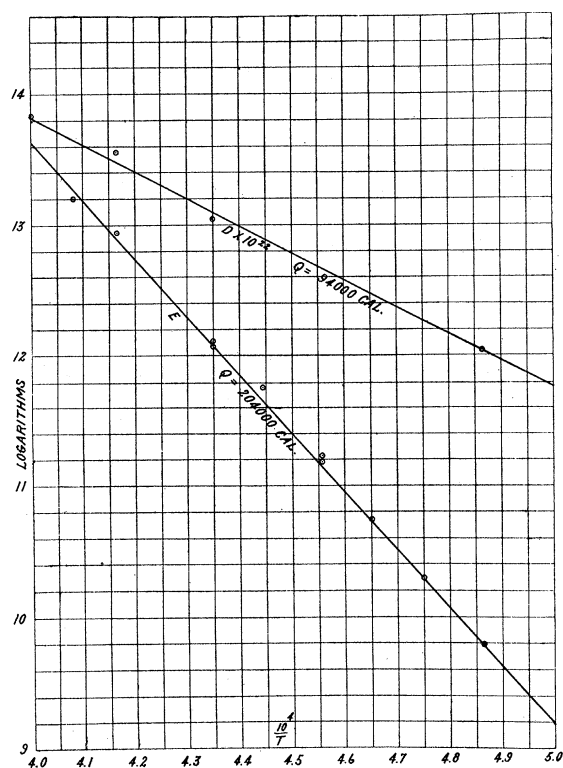


Fig. 7. Evaporation and diffusion of thorium as functions of temperature.

enormous ratio between the emission from active and deactivated filaments, that if a very short section of the filament retains its thorium, serious errors may arise in the determination of θ particularly for low values of θ . With filaments in a fairly active condition low testing temperatures such as 1450° can conveniently be used. Since the cooling effect of the leads is much more pronounced at these low temperatures than at the higher temperatures at which deactivation occurs, there is no appreciable emission from end portions of the filament which may have retained their thorium. At the higher testing temperatures used

with the low values of θ , more serious errors may occur. In future experiments all these difficulties can be avoided by dividing the anode into sections on the guard-ring principle.¹⁵

The general results of these runs with low values of θ are as follows. At temperatures from 2200° to 2250° E did not seem to fall off in value as θ decreased from 0.3 to 0.07 but showed a slight tendency to rise. At higher temperatures E did decrease with θ , the more rapidly the higher the temperature, but even at 2400° decreased less rapidly than in proportion to θ . As a result of these variations of E the temperature coefficient of E , and the heat of evaporation, are less than at higher values of θ .

The activation runs such as those of Tables I and II furnish some data on evaporation at high values of θ . Assuming E to be a linear function of θ , we see by Eq. (7) that the value of E for $\theta=1$ is $\nu_0 + \nu$, and this may be denoted by E_1 . Then Eq. (14) takes the form

$$1 - \theta_\infty = E_1 / N_0 k \quad (42)$$

Therefore $(1 - \theta_\infty)$ plotted against $1/k$ should give a straight line passing through the origin. The observed values of θ_∞ in Table II fulfil this condition satisfactorily. The slope of the line gives E_1/N_0 from which we find $E_1 = 1.66 \times 10^{10}$. The 6th Column of Table II contains values of θ_∞ calculated by Eq. (42) with this value of E_1 and the data for k in Col. 4. The agreement with the observed values is probably within the experimental error and justifies the assumption of a linear relation between E and θ in the region from $\theta=0.94$ to 1.0. The value of E_1 from the data of Table II is 2.75 times greater than the value of E calculated from Eq. (41) for this temperature (2055°).

The data in Columns 4 and 5 of Table I were also used to calculate values of E_1 by Eq. (42). These were compared with E calculated for the same temperatures from Eq. (41) and were found on the average to be 3.12 times greater. Col. 6 Table I contains values of θ_∞ calculated by Eq. (42) from the data for k in Col. 4 by placing $E_1 = 3.12E$ where E was calculated by Eq. (41) for the temperature T_a (Col. 2). The agreement between the observed and calculated values of θ_∞ is excellent. This is of especial significance when it is remembered that the data of Table I were obtained with a filament containing 1.5 per cent of thoria while the filament of Table II had 1.0 per cent.

The work at low, intermediate, and high values of θ thus leads to the following conclusions. In the range from $\theta=0$ to about 0.1, E increases probably about in proportion to θ , but before 0.2 is reached increases much more slowly. Between 0.2 and 0.8, E is approximately constant,

¹⁵ Langmuir and Kingdon, *Science*, **57**, 58 (1923)

showing however a tendency to increase slightly with θ at temperatures as high as 2400°, but to decrease slightly as θ increases at temperatures as low as 2200°. Above 0.8, E increases again and between 0.85 and 1.0 it increases linearly with θ until at $\theta=1$, E is about 3 times as great as in the range from 0.2 to 0.8.

Variation of heat of evaporation with θ . Dushman¹⁶ has proposed the following empirical equation for the velocity of monomolecular reactions

$$\frac{d \log c}{dt} = \nu e^{-h\nu/kT} \quad (43)$$

where c is the concentration of the reacting substance, and $h\nu$ is the heat of reaction per molecule. Although this equation is certainly not rigorous it has been found to apply with a satisfactory degree of approximation to many fundamental processes which depend on temperature. The first member of the equation is the reciprocal of the *average life* τ of the molecules of reacting substance, and in this form the equation becomes applicable to many classes of phenomena for which we have previously had no similar relation.

The average life of a thorium atom on a surface of tungsten is given by

$$\tau = N_0\theta/E \quad (44)$$

Combining these equations and substituting $Q = Nh\nu$, where Q is the heat of evaporation of thorium from tungsten per gram atom, we obtain

$$E = (N_0Q\theta/Nh)e^{-Q/RT} \quad (45)$$

When the values of N_0 , N and h are substituted in this equation it becomes

$$E = 1.804 \times 10^{17} Q\theta e^{-Q/RT} \text{ (atoms sec.}^{-1} \text{ cm}^{-2}\text{)}. \quad (46)$$

We may now calculate the value of Q as a function of θ from our data on the rate of evaporation as illustrated in Table VII. The second column gives the rate of evaporation at 2300° calculated from Eq. (41) which merely summarizes the experimental data. The value at $\theta=1$ is made 3 times that in the range 0.2 to 0.8 in accordance with our

TABLE VII
Heat of evaporation of thorium as a function of θ ; filament temperature 2300°K

θ	Rate of evaporation E (atoms sec. ⁻¹ cm. ⁻²)	Heat of evaporation Q (calories per g-atom)
0.2	1.22×10^{12}	182,800
0.5	1.22 "	187,100
0.8	1.22 "	189,200
1.0	3.66 "	185,200

¹⁶ S. Dushman, J. Amer. Chem. Soc., **43**, 397 (1921)

previous conclusion. The 3rd Col. gives values of Q calculated from these data by Eq. (46) but converted to calories per gram atom.

Considering the approximate nature of the Dushman equation the agreement between the calculated values of Q and the value $Q=204,000$ found more directly from Eq. (41) is satisfactory. It is probable that the differences in Q for different values of θ are accurate to much higher degree. Almost the same differences may be calculated from the same data by the Boltzmann equation. The most noteworthy feature of these variations of Q with θ is that they are so small. It indicates that the forces acting between adjacent thorium atoms on the surface is very small compared to those involved in holding these to the underlying tungsten atoms. The increase in Q between 0.2 and 0.8 corresponds to attractive forces while the decrease between 0.8 and 1.0 is evidence that the atoms are subjected to repulsive forces by the neighboring thorium atoms when they become more crowded. The effects are so small, however, that they prove that the thorium atoms are not closely packed. The results are thus in accord with the conclusion we have reached in regard to the magnitude of N_0 .

Volmer and Estermann¹⁷ have shown that mercury atoms that condense on a solid mercury crystal may retain their mobility of thermal agitation in an adsorbed film, as a kind of 2-dimensional gas. It is highly probable that thorium atoms on a tungsten surface at sufficiently high temperature are able in a similar way to move over the surface. The phenomena of induced evaporation, however, seem to indicate that this degree of mobility is very limited, for a thorium atom coming from within the filament to a surface only partly covered with thorium, would otherwise be able to push a thorium atom on the surface into an adjacent position instead of *inducing* it to evaporate. The average life of a thorium atom in a *given position* on the tungsten surface lattice (with respect to surface mobility) must therefore be long compared to the life of a thorium atom (with respect to evaporation) which has a *thorium atom* under it.

A summary of the properties of thoriated tungsten filaments is contained in Table VIII. With any such filament we may classify the phenomena into 2 groups: (I) those characteristic of the stationary state in which the metallic thorium is diffusing out of and leaving the filament at the same rate as it is produced within the filament by reduction of thoria, and (II) transient phenomena due to departures from the stationary state caused by changes in temperature or removal of thorium from the surface of the filament by sudden flashing or positive ion

¹⁷ Volmer and Estermann, *Zeitschr. f. Physik*, **7**, 1 and 13, (1921)

bombardment. These transient phenomena are of two kinds: (IIa) Those in which the rate of production of thorium metal in the filament is not equal to the rate of diffusion to the surface (so called steady state), and (IIb) Those in which the rate of evaporation from the surface is not equal to the rate of arrival at the surface.

TABLE VIII

Properties of a thoriated tungsten filament in the steady state

Filament contains 1 per cent of ThO ₂				Diameter 0.00389 cm		
(1)	(2)	(3)	(4)	(5)	(6)	(7)
<i>T</i>	<i>G_r</i>	<i>θ_r</i>	Electron emission <i>i_r</i>	Life <i>τ</i>	Time of recovery <i>1/a</i>	Time of activation <i>1/k</i>
	(atoms cm ⁻⁴)		(amp. cm ⁻²)	(hours)	(sec.)	(sec.)
1300°K	6.61 × 10 ¹⁷	0.99997	4.14 × 10 ⁻⁴		1.50 × 10 ¹⁰	
1400	2.23 × 10 ¹⁸	0.99975	3.12 × 10 ⁻³		1.11 × 10 ⁹	1.43 × 10 ¹¹
1500	6.41 × 10 ¹⁸	0.99878	0.0179		1.17 × 10 ⁸	5.23 × 10 ⁹
1600	1.61 × 10 ¹⁹	0.99528	0.0812		1.63 × 10 ⁷	2.88 × 10 ⁸
1700	3.64 × 10 ¹⁹	0.9848	0.287		2.86 × 10 ⁶	2.15 × 10 ⁷
1800	7.51 × 10 ¹⁹	0.9605	0.772	720,000	6.10 × 10 ⁵	2.02 × 10 ⁶
1900	1.43 × 10 ²⁰	0.9191	1.59	94,000	1.53 × 10 ⁵	2.18 × 10 ⁵
2000	2.57 × 10 ²⁰	0.8713	2.89	15,100	44,100	2.48 × 10 ⁴
2100	4.36 × 10 ²⁰	0.781	3.43	2,897	14,300	9.48 × 10 ³
2200	7.03 × 10 ²⁰	0.551	1.24	643	5,130	2.10 × 10 ³
2300	1.09 × 10 ²¹	0.139	0.114	164	2,010	531.
2400	1.63 × 10 ²¹	0.0601	0.168	47	855	7.0
2500	2.36 × 10 ²¹	0.0355	0.357	14.6	389	1.28
2600	3.31 × 10 ²¹	0.0207	0.774	5.01	191	0.268
2800	6.08 × 10 ²¹	0.0088	3.48	0.74	51	0.0161
3000	1.03 × 10 ²²	0.0041	13.5	0.14	17	0.0014

Col. 2 in the table gives values of G_r (the concentration gradient at the surface when the stationary state (I) has been reached) calculated by Eq. (35). Col. 3 gives θ_r , the fraction of the surface covered with thorium when the filament is in the stationary state (I). These data are calculated by means of Eq. (12), θ_∞ being replaced by θ_r and G by G_r . The values of D are taken from Table IV or Eq. (34). In accord with the experimental data discussed previously, the following convention has been adopted for values of ν_0 and ν .

Range of θ	ν_0	ν
0.0 to 0.1	0	10 E
0.1 to 0.85	E	0
0.85 to 1.0	-10.33 E	+13.33 E

The value of E is given by Table IV or Eq. (41).

Col. 4 gives the electron emission i_r in amperes per cm² at the temperature T (Col. 1) when the fraction θ_r of the surface is covered with thorium.

Dushman¹⁸ has shown that the electron emission from any heated metal is given by

$$i = 60.2T^2\epsilon^{-b/T} \text{ amp. cm}^{-2}, \quad (47)$$

where b is a constant which depends on the material of the cathode or the condition of its surface.

Eq. (2) may be written

$$b = b_0 + \theta(b_1 - b_0) \quad (48)$$

Dushman has obtained the values: $b_0 = 52,600$, $b_1 = 34,100$. Substituting these in Eq. (48) and then placing the value of b in Eq. (47) we obtain the data given in Col. 4.

The "stationary" emission from a thoriated filament thus reaches a maximum somewhat above 2000° and then falls gradually to that of pure tungsten.

Col. 5 gives the life of the thoria in the filament calculated from p_r (Eq. (37)) by the relation $\tau = 1.22 \times 10^{17}/p_r$. This represents the time required for the total thoria content of the filament to fall to one ϵ th of its original value.

Col. 6, under the heading Time of recovery, gives the time required for transient effects of the first class (IIa) to fall to one ϵ th of their value. Thus if the filament has been kept at 2000° until the stationary state has been reached, and the temperature is then changed to 2100° , G begins to change from the value 2.57×10^{20} and approaches the new stationary value 4.36×10^{20} , in such a manner that it takes 2897 seconds to go to within one ϵ th of the way to the final value. The quantity α , whose reciprocal is the time of recovery, is calculated and defined by Eqs. (23) and (24). The time of recovery gives a measure of the time needed to bring the filament into the stationary state.

The last column of the table gives the time of activation, the reciprocal of the rate of activation k , defined by Eq. (10). The values in the table were calculated by means of Eq. (11), replacing G by G_r . This time of activation is the time needed for θ or i to return to within one ϵ th of the way back to the "steady" value (θ_∞ or i_∞) after any small change produced by altering the temperature for such a short time that G_r is not appreciably affected. The time of activation is also a measure of the sensitiveness of the filament to effects which tend to destroy the thorium film on the surface, such as positive ion bombardment or chemical action of residual gases.

The data of Table VIII apply strictly only to a filament of the diameter given. By Eq. (36) we see that G_r should increase in proportion to R

¹⁸ Dushman, Phys. Rev. **20**, 109 (1922), and Gen. Electric Rev. **26**, 154 (1923)

and this will change θ_r and i_r . The life τ is independent of R . By Eq. (24) it appears that the time of recovery is proportional to R^2 , and by Eq. (11) the time of activation is inversely proportional to R at low temperatures and independent of R at high temperatures.

By introducing carbon into the filament, as for example by heating the filament in hydrocarbon vapors at low pressure, the value of G_r may be greatly increased, causing a corresponding increase in θ_r and i_r but a decrease in the life and in the time of activation. The decreased sensitiveness to gas effects may be of very great advantage in practical devices utilizing this type of cathode.

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