

## THE EVAPORATION OF THORIUM FROM TUNGSTEN

BY MARY R. ANDREWS

## ABSTRACT

The rate of evaporation of thorium from pure tungsten and from carbonized tungsten was measured between 2000° and 2500°K. The thorium was deposited on these surfaces by evaporation either from thoriated filaments or from metallic thorium. Evaporation from both surfaces was found to vary directly with the fraction covered, being more rapid from pure tungsten than from carbonized tungsten. Heat of evaporation from tungsten was calculated to be 177000 cal/gr-atom and from carbide 202000 cal.

THE evaporation of thorium from a tungsten surface has been determined by Langmuir<sup>1</sup> by measuring the rate of loss of electron emission power of a filament containing thorium; but such a measurement is complicated by the diffusion of thorium to the surface from the interior of the filament so that the change in electron emission depends on two factors: (1) the loss of thorium from the surface by evaporation, and (2) the replacement of the thorium on the surface by diffusion from within the filament.

It was thought, therefore, worth while to make a few experiments in which thorium deposited from external sources on pure tungsten was allowed to evaporate. The experiments were performed with tubes which contained four filaments. The two middle ones were hairpins of four mil pure tungsten wire ten centimeters long. In most of the experiments the two outer filaments were of 8.5 mil tungsten containing two percent of thoria. In a few, however, tungsten coils surrounding short rods of metallic thorium were used. Filaments were spaced about a centimeter apart. After degassing, one of the middle filaments was carbonized by running it at incandescence in a very low pressure of naphthalene vapor.

Great precautions were taken to produce a good vacuum. The filaments were welded to heavy molybdenum leads and thoroughly degassed. The anode was a calcium mirror deposited on the walls of the tube from a piece of wire heated by a tungsten spiral in the lower end of the tube, and connected to the main tube was a side tube containing degassed absorbent charcoal which was immersed in liquid air during the experiments.

It was found very difficult to maintain emission at temperatures at which evaporation of thorium was negligible, with voltage on the anode, when the tube was connected to the pumping system or was trapped off by a mercury trap and liquid air trap. The following data, therefore, were obtained after the tubes were sealed off the exhaust system. The persistence of emission at temperatures below 2000°K was used as a test of good vacuum in these tubes. If not successful at first, it was usually so after the second deposition of thorium, the evaporation and redeposition of thorium and

<sup>1</sup> Langmuir, Phys. Rev. **22**, 357 (1923).

tungsten being an excellent way to clean up residual gas. The effect of gas was much more marked on the uncarbonized than on the carbonized filaments.

Temperatures of uncarbonized filaments were controlled by their watts input. These were calculated from Forsythe's and Worthing's<sup>2</sup> data for watts/cm<sup>2</sup>. Correction for cooling of the ends was made according to the cooling curve published by Dushman and Ewald<sup>3</sup> except that twice the published value for  $\Delta V$  was used, this value having been found by the authors to have been determined for one lead only. The carbonized filaments were run at twenty percent greater energy input than calculated for an uncarbonized filament. This factor (1.2) is an average of a number of photometric determinations made by the author some years ago. Carbonized filaments vary considerably in their emissivity depending on the state of the carbonized surface, so that there is a probability of some error in the case of any particular filament. The carbonized filaments in these experiments were prepared under as nearly the same conditions as possible, but the irregularity in the results may be laid to these unavoidable inaccuracies in temperature.

It was found necessary to run the two thoriated wires for an hour or more at 2800°K in order to cover the surface of the middle filaments completely enough (eight-tenths or more) to give a satisfactory emission. After such a deposition, when the emission from either of the middle (coated) wires was studied, it was found to increase at first quite rapidly at any constant filament temperature between 1800° and 2200°. It is assumed that this activation is due to the fact that some tungsten is evaporated from the thoriated filaments, and deposits on the test filaments along with the thorium. During the first few minutes of heating such a filament, therefore, the deposited atoms become rearranged, the thorium diffusing outward to form a more or less complete surface layer, and undoubtedly also diffusing to a slight extent down into the tungsten. This diffusion inward might be a disturbing factor in that later, during the evaporation of the surface layer, it would be possible that some thorium might again come to the surface and replace that which has evaporated. Since, however, an extremely thin layer (probably not over ten atoms thick) was deposited and since all the thorium atoms coming to the surface under other thorium atoms would immediately cause the evaporation of these atoms, it is easily seen that the diffusion of thorium atoms would be almost completely toward the surface and that the layer deposited would be very quickly exhausted of thorium, leaving only a monatomic adsorbed layer on the surface.<sup>4</sup>

The procedure followed in determining the rates of evaporation, therefore, was (1) deposition of thorium and tungsten from the thoriated filaments or from the metallic thorium on the pure tungsten filament and carbonized filament, (2) running one of the coated filaments at, say, 2000°, until activation had reached a maximum, (3) running this filament at a known tempera-

<sup>2</sup> Worthing, *Astrophys. J.* **61**, 129 (1925).

<sup>3</sup> Dushman and Ewald, *G. E. Review* **26**, 154 (1923).

<sup>4</sup> For the mechanism of the formation of a thorium covered surface see Langmuir, reference 1.

ture and measuring the decline in emission with time. Emission measurements were made at 1500°K. After both filaments had been so tested, they were

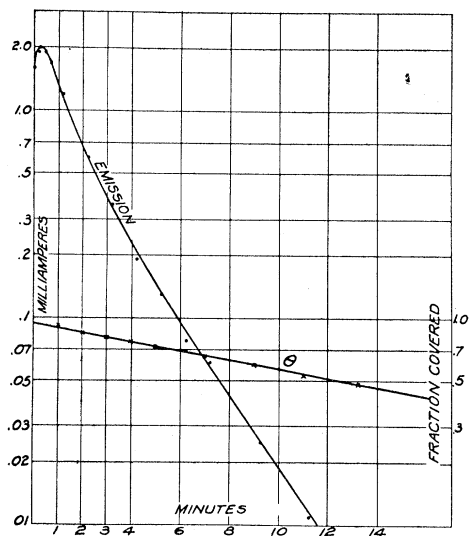


Fig. 1. Evaporation of thorium from carbonized tungsten at 2400°K.

run at a somewhat higher temperature (the carbonized filament not over 2500°) until the emission had fallen to the value for pure tungsten, the deposition of thorium was again made, etc.

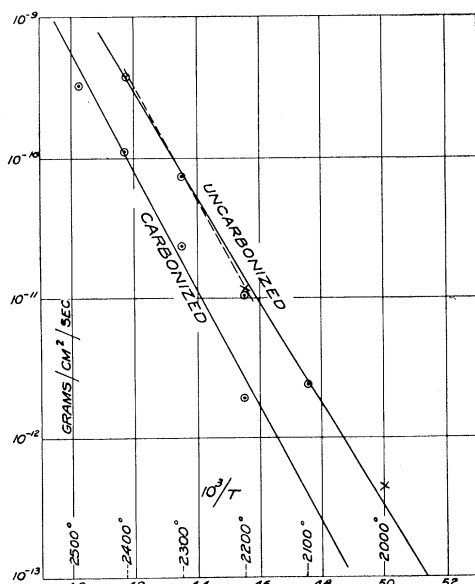


Fig. 2. Rate of evaporation of thorium vs. temperature.

Fig. 1 shows a characteristic evaporation curve. In this case it is obvious that the preliminary activation had not been quite complete.

At 1500° the emission from this filament if completely covered with thorium should be 4.00 milliamperes.<sup>5</sup> From the pure tungsten surface the emission at 1500° is 0.018 microamperes.<sup>6</sup> From these data, and the above evaporation curve, the fraction of the surface covered ( $\theta$ ) at any instant is easily calculated.<sup>1</sup>

The straight line in Fig. 1 marked  $\theta$  shows that the surface of thorium decreases logarithmically with time. The slope of this line  $d \log \theta/dt$  gives the rate of evaporation or the fraction of the surface covered which evaporates in one second.

Table I gives in column two values of  $d \log \theta/dt$  for carbonized and uncarbonized filaments at various temperatures. Assuming that there are  $0.756 \times 10^{15}$  atoms of thorium per square centimeter, the grams of thorium and the number of atoms evaporated per second from a completely covered surface can be calculated. These values are given in columns 3 and 4 and the former shown in Fig. 2. It is of interest to note that they are not very different from the values for the evaporation of tungsten as given by Jones, Langmuir and Mackay.<sup>7</sup> They report  $1.25 \times 10^{-11}$  grams/cm<sup>2</sup> at 2200° and  $4.36 \times 10^{-10}$  at 2400°. The tungsten data are shown on Fig. 2 by the dotted line.

TABLE I. *Evaporation of thorium at various temperatures.*

Temperature	d log $\theta$		Evaporation atoms/cm <sup>2</sup> sec.
	dt	grams/cm <sup>2</sup> sec.	
Uncarbonized filaments			
2100°K	$8.4 \times 10^{-6}$	$2.45 \times 10^{-12}$	$6.35 \times 10^9$
2200	$3.7 \times 10^{-5}$	$1.08 \times 10^{-11}$	$2.8 \times 10^{10}$
2300	$2.5 \times 10^{-4}$	$7.29 \times 10^{-11}$	$1.9 \times 10^{11}$
2400	$1.3 \times 10^{-3}$	$3.79 \times 10^{-10}$	$.98 \times 10^{12}$
*2000	$1.5 \times 10^{-6}$	$4.4 \times 10^{-13}$	$1.1 \times 10^9$
*2200	$4.0 \times 10^{-5}$	$1.17 \times 10^{-11}$	$3.0 \times 10^{10}$
Carbonized filaments			
2200°K	$6.6 \times 10^{-6}$	$1.92 \times 10^{-12}$	$5.0 \times 10^9$
2300	$8.5 \times 10^{-5}$	$2.38 \times 10^{-11}$	$6.4 \times 10^{10}$
2400	$3.8 \times 10^{-4}$	$1.11 \times 10^{-10}$	$2.9 \times 10^{11}$
2485	$1.14 \times 10^{-3}$	$3.32 \times 10^{-10}$	$.86 \times 10^{12}$

\* Thorium deposited from metallic thorium

From the above values, using the Clapeyron-Clausius equation in the form

$$Q = 2.303 R [d \log P / d(1/T)]$$

the heat of evaporation of thorium can be calculated. For evaporation from pure tungsten  $Q = 177000$  calories per gram atom, from carbonized tungsten it is 202000 calories. Langmuir's value for evaporation of thorium from tungsten is 204000 calories. For evaporation/cm<sup>2</sup> his figures are three to nine times those of the author.

<sup>5</sup> Dushman and Ewald, Phys. Rev. **29**, 857 (1927).

<sup>6</sup> Dushman, Rowe, Ewald and Kidner, Phys. Rev. **25**, 338 (1925).

<sup>7</sup> Jones, Langmuir and Mackay, Phys. Rev. **30**, 201 (1927).

The results given above differ from those of Langmuir<sup>1</sup> in one essential. He found that the rate of evaporation of thorium at constant temperature was constant independent of the fraction of the surface covered except where this fraction was very small. This was considered to be due to the attraction of the thorium atoms for each other, so that when the surface was almost completely covered and the thorium atoms were in contact with each other, they tended to hold one another in place. Hence the fraction of thorium atoms evaporating increased as the surface became less completely covered. The author's data show a rate of evaporation which is a linear function of the surface covered, i.e., a constant fraction of the amount of thorium on the surface, indicating that the attraction between the thorium atoms is negligible at the temperatures used.

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RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY,  
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