THE PHOTOELECTRIC PROPERTIES OF TANTALUM

By Alvin B. Cardwell
Department of Physics
University of Wisconsin

(Received October 27, 1931)

Abstract

Tantalum was carefully outgassed and it's photoelectric properties studied after stable conditions were reached. Heating 1000 hours at temperatures up to 2200°K produced an apparent stable condition of the surface. Curves, showing the variation of the photoelectric current as a function of the temperature, are plotted for different wave-lengths. For wave-lengths near the threshold, there is a great increase in the photoemission with increasing temperature. With decreasing wave-lengths, this variation becomes very much smaller. Extrapolated values from the $F(\lambda)$ curves show the long-wave limit to be at 20°C, 2750A; and at 700°C, 2825A. Further heat treatment at temperatures up to 2500°K produced a final stable condition. Here again are plotted curves showing the variation of the photoelectric current as a function of the temperature for different wave-lengths. In this case, the great increase in the photoelectric sensitivity with temperature for wave-lengths near the threshold becomes smaller as the wave-lengths used decreases, finally reaching negative values for wave-lengths more than 300A shorter than the threshold value. Extrapolated values from $F(\lambda)$ curves taken at 293°K and 973°K show the long-wave limit at the respective temperatures to be 3050A and 3160A. From curves plotted according to Fowler's theory, the true threshold wave-lengths were found to be as follows: (1). For tantalum in first apparent stable condition (average = 2742A (4.50 volts). (2). For tantalum in final stable condition (average) = 2974A (4.15 volts).

IN A recent paper Professor R. H. Fowler[1] developed a theory for the effect of temperature on the photoelectric sensitivity of a clean metal near the threshold. As a part of the experimental evidence offered in substantiation of the theory the writer was delighted to supply Professor Fowler with some data on tantalum which, although taken more than a year ago, had never been published. The present paper is a report of these results along with a description of the photoelectric and gas characteristics of the metal as it went through a very extensive outgassing process.

Apparatus

The apparatus used in the present work was only slightly different from that used by numerous other investigators. A schematic diagram of the experimental tube and ionization gauge is shown in Fig. 1. The strip to be tested consisted of a ribbon of tantalum 0.03 mm thick, 4 mm wide, and 18 cm long, suspended in the form of a loop by the tungsten leads W. C is a molybdenum receiving cylinder connected by means of a flexible molybdenum lead to the collecting electrode L. The quartz window Q is sealed directly to the Pyrex

[1] Fowler, Phys. Rev. **38**, 45 (1931).

tube by means of a graded joint. Just opposite this window is a circular opening in the cylinder. By means of a magnetically controlled iron door this opening could be covered while the sample was being heated to high temperatures. This prevented the distillation of metal onto the quartz window. The insulated ring G supported by the heavy tungsten wire T was always kept at the same potential as C. Thus it was possible to measure only the current from the portion of the loop which had been subjected to a rather uniform heat treatment. The ionization gauge is of the general type described by Dushman and Found.[2]

Photoelectric currents were measured by a Compton quadrant electrometer having a sensitivity of 30,000 mm per volt. A high resistance made of

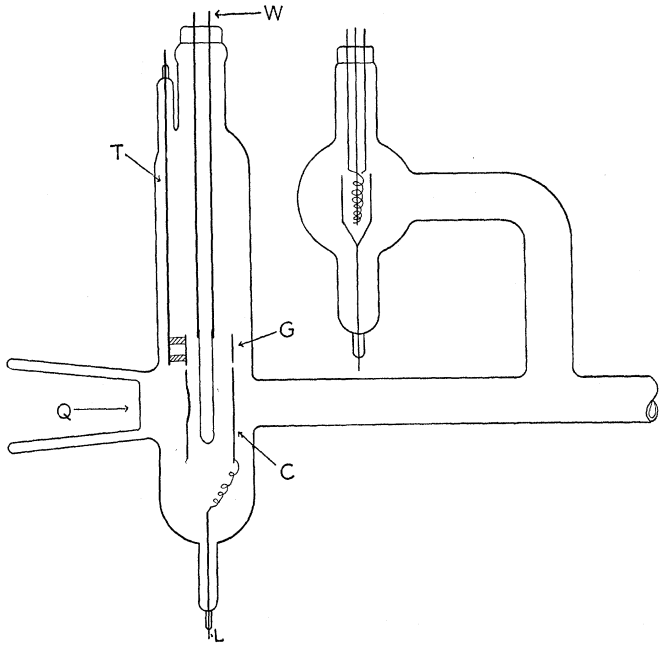


Fig. 1. Diagram of apparatus.

fused soda glass and cupric oxide[3] was shunted across the quadrants so that the steady deflection method could be used.

During a great part of the outgassing period the source of light was the undispersed radiation from a vertical Cooper-Hewitt quartz mercury arc. For a study of the characteristics during the latter part of the period, a Bausch and Lomb quartz single monochromator was placed between the arc and the tantalum sample. Mr. J. H. Dillon[4] had made a study of the particular monochromator used, finding that the impurity of the dispersed radiation (with slit widths 0.02 mm) was not sufficient to produce appreciable errors in

[2] Dushman and Found, Phys. Rev. **23,** 743 (1924).
[3] Andrewes, Davies, and Horton, Proc. Roy. Soc. **A117,** 649 (1928).
[4] Dillon, Phys. Rev. **38,** 408 (1931).

the $F(\lambda)$ curve. The relative intensities of the mercury lines were determined by a thermopile connected to a Leeds and Northrup low resistance galvanometer.

Temperatures were measured by an optical pyrometer of the disappearing filament type, which had been calibrated by observations upon the gold point and the palladium point. Black-body temperatures were corrected for the emissivity of tantalum according to data by Mendenhall and Forsythe.[5]

The tantalum filaments, obtained from the Fansteel Company of North Chicago, were made from a very pure sample of the metal.

Procedure and Results

The receiving cylinder was placed in an auxiliary vacuum system where it was heated to 900°C for five days by electronic bombardment. It was then transferred to the experimental tube and sealed in the vacuum system with the sample. The tube and gauge were then encased in an electric furnace and baked for 20 days at 500°C. During the last fourteen days of this interval the filament was heated by a conduction current at temperatures which were slowly increased up to 1400°C.

At the end of this twenty-day period the furnaces were removed and the tube was properly shielded for photoelectric observations. The full arc sensitivity varied a great deal, and in a most irregular fashion, during the next few hundred hours of heat treatment. It was only after approximately 1000 hours of heat treatment at temperatures up to 2200°K that the sample showed indications of becoming photoelectrically stable. This is, (1) no further change in its full arc sensitivity resulted with 100 additional hours of heat treatment at the same temperature, and (2) during a one-hour interval no fatigue was observed. At this point attention should be called to the fact that, although the latter condition has been found up to the present to be characteristic only of surfaces which seemed to be gas-free, the surface in this case was not gas-free. This point will be clarified in what follows.

While the sample was in the somewhat stable condition described above, the monochromator was adjusted so that a further study could be made. Fig. 2 shows the $F(\lambda)$ curves for two temperatures. The extrapolated values for the threshold wave-length at the two temperatures have been indicated in the figure. A study of photoelectric sensitivity for individual lines as a function of the temperature is shown in Fig. 3. It is quite obvious that the curves in Figs. 2 and 3 are entirely consistent and that an $F(\lambda)$ curve for any temperature within the range covered can be plotted from the data used in obtaining the curves in Fig. 3.

After several curves, identical with those reproduced in Figs. 2 and 3, were taken, the temperature of the sample was increased to 2300°K. Heating 12 hours at this temperature produced a shift in the threshold toward the red. Fifty hours' additional heat treatment at temperatures up to 2500°K produced no further change in the photoelectric characteristics. It is therefore believed that the metal in this condition was gas-free.

[5] Mendenhall and Forsythe, Astrophys. J. **37**, 380 (1913).

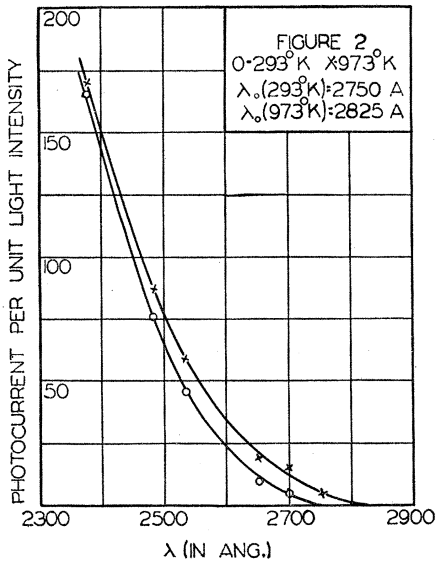


FIGURE 2
0-293° K X-973° K
λ₀(293°K)=2750 A
λ₀(973°K)=2825 A
PHOTOCURRENT PER UNIT LIGHT INTENSITY
200
150
100
50
2300
2500
2700
2900
λ (IN ANG.)

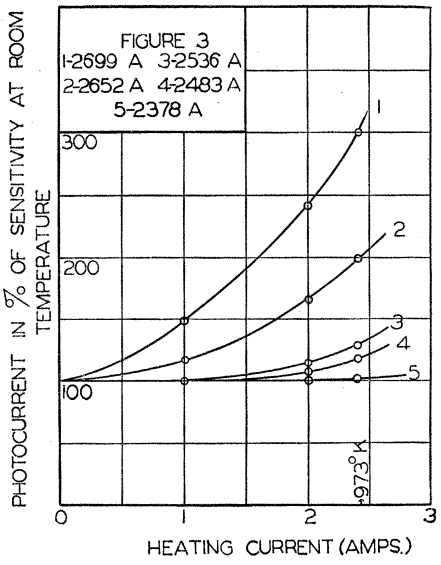


FIGURE 3
1-2699 A 3-2536 A
2-2652 A 4-2483 A
5-2378 A
PHOTOCURRENT IN % OF SENSITIVITY AT ROOM TEMPERATURE
300
200
100
1
2
3
4
5
973° K
0
1
2
3
HEATING CURRENT (AMPS.)

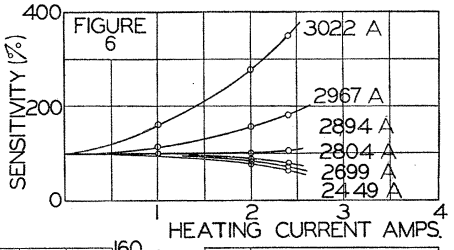
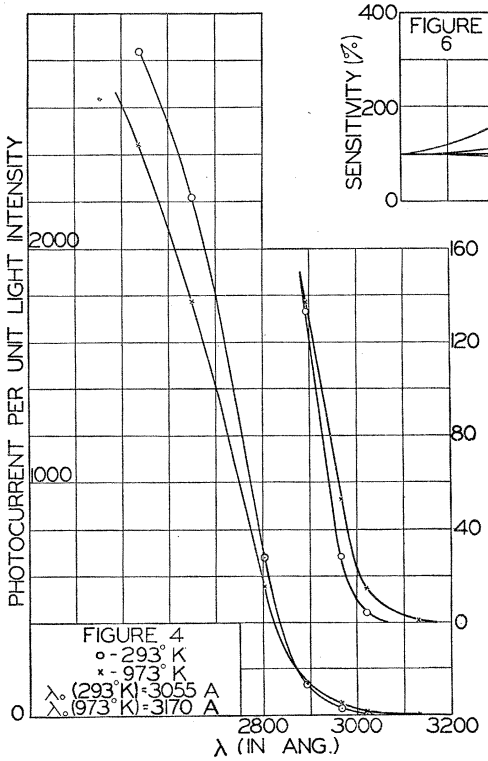


FIGURE 6
SENSITIVITY (%)
400
200
0
3022 A
2967 A
2894 A
2804 A
2699 A
2449 A
1
2
3
4
HEATING CURRENT AMPS.


PHOTOCURRENT PER UNIT LIGHT INTENSITY
2000
1000
0
160
120
80
40
0
FIGURE 4
o - 293° K
x - 973° K
λ₀ (293° K)=3055 A
λ₀ (973° K)=3170 A
2800
3000
3200
λ (IN ANG.)

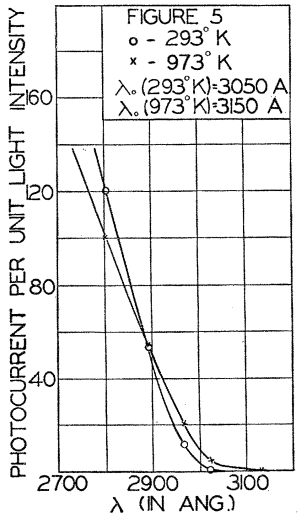


FIGURE 5
o - 293° K
x - 973° K
λ₀ (293° K)=3050 A
λ₀ (973° K)=3150 A
PHOTOCURRENT PER UNIT LIGHT INTENSITY
160
120
80
40
2700
2900
3100
λ (IN ANG.)

The data for the $F(\lambda)$ curves in Figs. 4 and 5* were taken after the sample had been subjected to this severe heat treatment. In Fig. 4 the points near the threshold are replotted on a much larger scale just above the regular curve. Again the extrapolated values for the threshold frequencies have been indicated in the figures. The crossing of the high and low temperature curves show that the variation of the photoelectric emission with temperature is quite different for various individual wave-lengths. Fig. 6 brings this out much more clearly.

In Fig. 5, the change in slope near the shorter wave-lengths suggests that the $F(\lambda)$ curves may be approaching a maximum value. This would be in agreement with the theoretical deductions of Wentzel,[6] Frohlich,[7] and Tamm

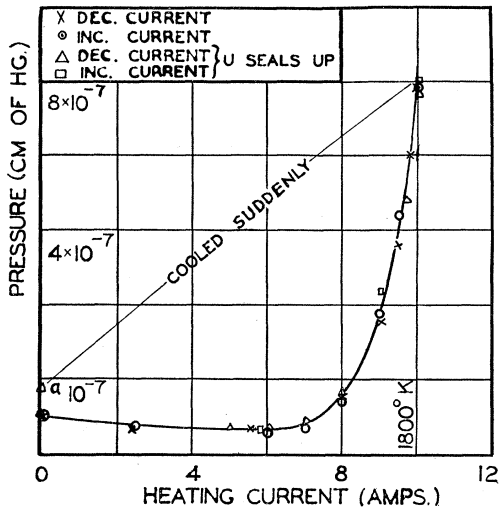


Fig. 7. Equilibrium pressure as a function of the heating current through the filament.

and Schubin[8] that in all cases such curves should have a maximum. Data for much shorter wave-lengths would be desirable to clarify this point.

Throughout the greater part of the outgassing process the pressures underwent rather striking changes as the temperature of the filament was changed. Fig. 7 is a characteristic curve showing the equilibrium pressure as a function of the heating current through the sample. It should be pointed out that one complete set of the data shown graphically was taken while the tube and gauge were "cut off" from the pumping system by means of a mercury U-seal. Clearly, the equilibrium pressure was identical in the two cases. It should also be stated that within wide limits the rapidity with which the heating current was changed made no difference in either the final equilibrium pressure or the time required to reach that pressure. Usually this

* Fig. 5 is identical with that reproduced by Fowler.

[6] Wentzel, Sommerfeld's Festschrift, p. 20 (1928).

[7] Frohlich, Ann. d. Physik **7**, 103 (1930).

[8] Tamm and Schubin, Zeits. f. Physik **68**, 97 (1931).

equilibrium value was reached within an interval of 12 seconds after the heating current was changed. In fact, in only one case was an exception to the above statement observed. The pressure 12 seconds after a heating current of 10 amperes was broken (thus allowing the sample to cool very rapidly to room temperature) was greater (point *a*, Fig. 7) than when the current was gradually decreased to zero during an interval of 30 seconds. When the sample was suddenly cooled, about 3 minutes elapsed before the pressure decreased to a value corresponding to that reached by the slower cooling process. Here again these values were practically independent of whether the U-seal was or was not closed.

TABLE I.

Temperature °K	λ (A)	Photo-current per unit light intensity	$h\nu/kT$	log I/T^2	log $I/T^{3/2}$	$h\nu_0/kT$	λ_0 (A)	Work function (volts) (Average)
(a) Sample in first apparent stable condition (Fig. 2)								
293	2699	5.0	181.0	−9.75	−6.91	—	Theory 1	
	2652	11.0	184.5	−8.96	−6.12	177.3	2750	
	2537	46.0	192.5	−7.53	−4.69	—		4.53
	2480	76.0	197.0	−6.93	−4.19	—	Theory 2	
	2376	166.0	206.0	−6.25	−3.41	179.3	2725	
973	2754	5.0	53.6	−12.15	−8.71	—	Theory 1	
	2699	14.5	54.6	−11.09	−7.65	53.5	2745	
	2652	20.0	55.6	−10.75	−7.32	—	—	4.49
	2537	59.0	58.1	−9.68	−6.24	—	Theory 2	
	2480	87.0	59.4	−9.27	−5.83	—	—	
	2376	170.0	62.1	−8.62	−5.18	53.4	2750	
(b) Sample in final stable condition (Fig. 4)								
293	3022	4.5	161.5	−9.856	−7.016	—	Theory 1	
	2967	28.7	164.6	−8.003	−5.163	163.0	3000	
	2894	133.0	169.0	−6.470	−3.630	—		4.12
	2804	680.0	174.3	−4.838	−1.998	—		
	2652	2220.0	184.5	−3.655	− .815	—	Theory 2	
	2537	2840.0	192.5	−3.409	− .569	163.5	2990	
973	3132	1.5	47.1	−13.355	−9.915	—	Theory 1	
	3022	14.5	48.7	−11.086	−7.646	50.0	2942	
	2967	53.0	49.7	−9.790	−6.350	—		4.19
	2894	137.0	50.9	−8.841	−5.401	—		
	2804	555.0	52.5	−7.442	−4.002	—	Theory 2	
	2652	1780.0	55.6	−6.276	−2.836	50.0	2942	
	2537	2440.0	58.1	−5.961	−2.521	—		
(c) Sample in final stable condition (Fig. 5)								
293	3022	1.0	161.5	−11.360	−8.520	—	Theory 1	
	2976	11.6	164.6	−8.909	−6.069	162.5	3005	
	2894	53.2	169.0	−7.386	−4.546	—	Theory 2	4.13
	2804	120.0	174.3	−6.573	−3.733	163.0	3000	
973	3132	.3	47.1	−14.965	−11.524	—	Theory 1	
	3022	4.5	48.7	−12.257	−8.816	49.5	2970	4.18
	2967	20.9	49.7	−10.721	−7.281	—		
	2894	53.3	50.9	−9.748	−6.308	—	Theory 2	
	2804	100.0	52.5	−9.155	−5.715	50.0	2942	

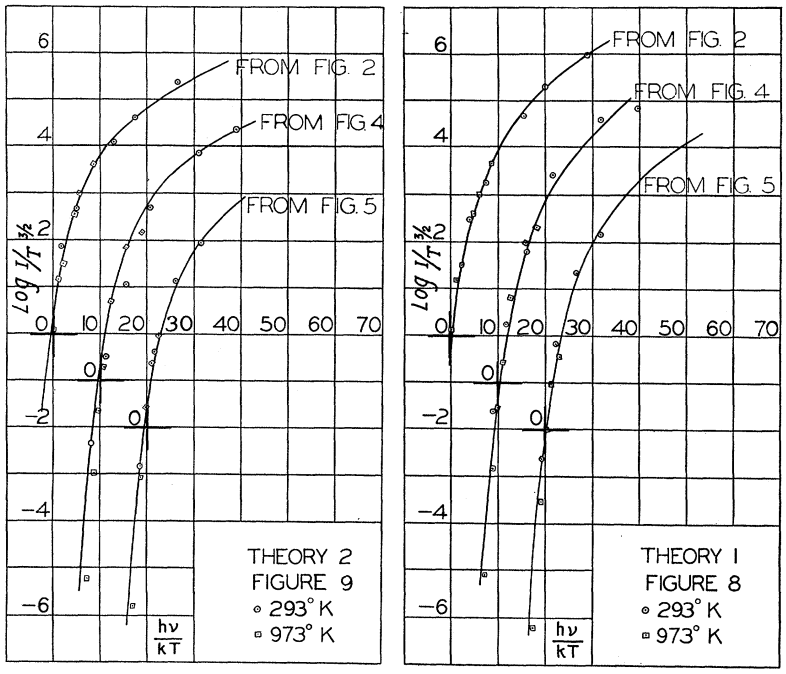
Data for the curves shown in Fig. 7 were taken after the sample had been outgassed 480 hours. With further heat treatment the equilibrium pressures became smaller and the pressure-heating current curves approached nearer and nearer a straight line with a zero slope. The pressure at the end of 1000 hours of heat treatment was 10^{-8} mm of Hg. This corresponds to a galvanometer deflection of only 1 mm. It is therefore impossible to say that the final pressures were *absolutely* independent of the temperature of the filament. A change of 10 to 15 percent could not have been detected.

Tantalum greedily absorbs hydrogen[9] when heated to redness, thus forming the hyride, and nitrogen[10] has been found to react with it at high temperatures (up to 1200°C) forming the nitride. Consequently, there is a possibility that the minimum value of the pressure in the pressure-temperature curve (See Fig. 7) is a direct result of one or both of these chemical actions.

The peculiar affinity of tantalum for hydrogen and nitrogen, and the gas characteristics reported herewith cast somewhat of a doubt as to the "cleanness" of the surface. It is quite possible that at least one, and perhaps both, of the stable conditions reported herewith are characteristic of tantalum with a stable compound on the surface. It is hoped that the thermionic data will give some additional information on this point.

Application of Fowler's Theory

In Fowler's paper, to which reference has already been made, the shift in the long-wave limit with temperature is completely accounted for by the change of the energy distribution of the electrons with temperature. A graphical method is given enabling the whole of the observed points near the threshold for all temperatures to be used in determining the "true threshold" wave-length. By true threshold is meant the threshold which would be observed if the metal were at absolute zero.



In Table I a summary of data from which such an analysis can be made is given. For Fowler's first theory the general method is as follows. First, the

[9] W. von Bolton, Zeits. f. Elektrochem. **11,** 47 (1905).

[10] W. Muthmann, Liebig's Ann. **355,** 62 (1907).

theoretical curve is plotted, then log I/T^2 is plotted against $h\nu/kT$, the scales of the log and $h\nu/kT$ being the same. The origin is then adjusted so as to bring as nearly as possible the observed points into coincidence with the theoretical curve and the points transferred to the theoretical curve. From the $h\nu/kT$ shift the threshold frequency, ν_0, is calculated. Exactly the same procedure is followed for theory 2 except in this case T^2 is replaced by $T^{3/2}$. Fig. 8 shows the curves obtained, on the basis of theory 1 as described above, from data taken on the metal while in both the first state of apparent stability and the final state of stability (Figs. 2, 4, and 5). Similar curves on the basis of theory 2 are reproduced in Fig. 9. The values of the threshold as determined by the shift in the abscissa are shown in Table I. The values for the metal in the final stable state (Figs. 4 and 5) are almost identical with Dushman's[11] value of 4.01 volts for the thermionic work function. In every case the general agreement of the actual points with the theoretical curves is quite good. It is interesting to note that the theory seems to hold to the same degree of accuracy for the metal in both the final state and first state of apparent stability (Figs. 2, 8 and 9).

Fowler[1] discussed the change in slope which leads to the intersection of the curves shown in Figs. 4 and 5, but was unable to arrive at any reasonable explanation. The fact that both gold[9] and silver[10] show a similar crossing, to a much less degree, however, leads one to believe that the effect is a normal one for clean metals. No crossing was observed for the metal while in its first apparent stable condition. There is, however, a possibility that the curves might have crossed had observation been made with much shorter wavelengths.

In conclusion, it is a pleasure to thank Professor Mendenhall under whose invaluable guidance the experiment was performed.

[11] Dushman, Phys. Rev. **25**, 338 (1925).