

## The Temperature Scale, Thermionics, and Thermatomics of Tantalum

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The energy cycle  $\varphi_0^- + \varphi_0^+ = \varphi_0^0 + V$  has been followed experimentally for tantalum. This involved a redetermination of the temperature scale with emissivity varying linearly from  $\epsilon_{\lambda T} = 0.439$  at  $T = 1200^\circ\text{K}$  to  $\epsilon_{\lambda T} = 0.384$  at  $T = 2400^\circ\text{K}$  for  $\lambda = 0.669\mu$ . Thermionic measurements of the electron work function and of the positive ion work function yielded, respectively,  $\varphi_0^- = 4.19$  ev and  $\varphi_0^+ = 10.0$  ev, with an electron emission constant  $A^* = 55$  amp.  $\text{cm}^{-2}$   $\text{deg}^{-2}$ . By a gain of weight method the work function of the neutral tantalum atom was found to be  $\varphi_0^0 = 7.97$  ev. The ionization potential of tantalum is not known but may be estimated to be about  $V = 7.3$  ev. These values fail to close the energy cycle by 1.1 ev which is believed to be outside the experimental uncertainty of the measurements.

### INTRODUCTION

IT may be shown that for a given metal the electron work function  $\varphi^-$ , the positive ion work function  $\varphi^+$ , the ionization potential  $V$ , and the work function of the neutral atom  $\varphi^0$  at any temperature are related by the equation

$$\varphi^- + \varphi^+ = \varphi^0 + V. \quad (\text{A})$$

This cycle has been followed experimentally for but a few metals (W, Mo, Cb), and the agreement of the measured values with the prediction of (A) is satisfactory except for the case of columbium. At the time this present program was initiated (1937) no data for tantalum on the temperature scale or on  $\varphi^-$ ,  $\varphi^+$ , or  $\varphi^0$  had appeared in the literature since the technique of high vacuum had been advanced to its present stage. Data on  $\varphi^+$ ,  $\varphi^0$ , and  $V$  were entirely lacking.

The purpose of this work has been to determine if the cycle closes for tantalum. To that end the temperature scale was redetermined, a new measure of the electron work function made, the positive ion work function obtained, and the thermatomic work function calculated from a "gain of weight" method.

### TEMPERATURE SCALE AND EMISSIVITY

The temperature scale for tantalum was determined by using the methods described by Wahlin.<sup>1</sup> A strip of the metal of 0.055-mm thickness was wrapped about a 3-mm diameter

<sup>1</sup>H. B. Wahlin and L. O. Sordahl, Phys. Rev. **45**, 886 (1934).

mandrel and welded to form a tube of 85-mm length. A 0.55-mm hole drilled into the center of the tube wall served as a blackbody of the same temperature as the tube itself. Stock tantalum<sup>2</sup> from the Fansteel Company was used for the emissivity cylinder, and in all the subsequent phases of this work. This tube filament was mounted in a glass envelope and evacuated. The envelope was baked at  $400^\circ\text{C}$  for 200 hours, and the filament outgassed at  $2000^\circ\text{K}$  for 1000 hours, with occasional 30-second flashings to  $2350^\circ\text{K}$ , until a final vacuum of  $4 \times 10^{-8}$  mm was obtained for temperatures below  $1800^\circ\text{K}$ .

The true temperature  $T$  of the tube was measured by sighting on the hole a disappearing filament optical pyrometer calibrated directly from gold-point melts in this laboratory, supplemented by the conventional rotating sector method for other temperatures. The brightness temperature  $T_B$  was found by sighting the pyrometer either side of the hole. The average spread of readings at any one temperature was less than  $0.5^\circ$ . Data were taken on two different specimens. The average deviation of an experimental point from the resulting  $T_B$  vs.  $T$  plot was less than  $1^\circ$ .<sup>3</sup>

<sup>2</sup>Of typical analysis Ta 99.9 percent, Fe 0.01 percent (max), C 0.003 percent (max).

<sup>3</sup>In connection with this work it was found the writer had an eye defect which caused his pyrometer readings to be at variance with those of several other observers, far outside the spread of the settings. Agreement was good with sources of large size such as the outside of the filament, but poor for sources of small size, such as the blackbody hole. Thus, in one typical instance Dr. R. W. Wright obtained  $1545.7^\circ\text{K}$  for the surface, and  $1650.7^\circ\text{K}$  for the hole, while the writer obtained  $1545.2^\circ\text{K}$  for the surface and  $1643.7^\circ\text{K}$  for the hole. This gave values for the emissivity of 0.415 and

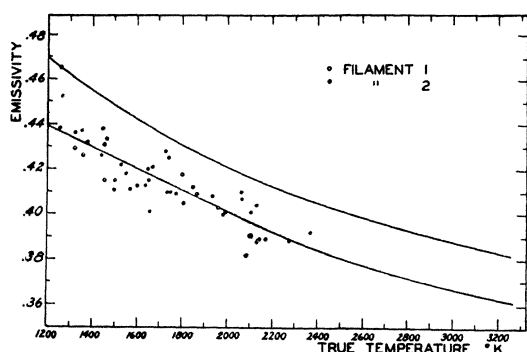


FIG. 1. The emissivity of tantalum at  $\lambda=0.669\mu$ . Upper plot is from data of Malter and Langmuir.

The emissivity  $\epsilon_{\lambda T}$ , of tantalum, was calculated from

$$\ln \epsilon_{\lambda T} = C_2/\lambda[(1/T) - (1/T_B)],$$

where  $C_2 = 1.4362$  cm deg. is the second radiation constant, and  $\lambda = 0.669\mu$  is the effective wavelength at which measurements of  $T$  and  $T_B$  were made.  $\epsilon_{\lambda T}$  was plotted as a function of  $T$  (see Fig. 1) and a straight line drawn through the mean of the experimental points. This plot was extrapolated beyond  $T = 2368^\circ\text{K}$  parallel to the emissivity data given by Malter and Langmuir.<sup>4</sup> The highest temperature at which the blackbody could be operated was  $2368^\circ\text{K}$ , and for higher temperatures  $T_B$  as a function of  $T$  was calculated from the emissivity curve.

0.438, respectively. Since the defect was the writer's all emissivity data were taken by R. W. W., and on all subsequent work care was taken that the image in the pyrometer was of sufficient size that the defect did not introduce an error in temperature measurements.

The defect may be explained if one postulates that the minimum retinal area required by the eye for intensity matches is greater for the writer than is normal. It is well known that brightness matches cannot be made accurately between point sources, but rather that the eye requires a certain image area as a minimum for significant comparison. This "minimum area" may well vary from one eye to the next. If that area should be larger than the size of the image of the pyrometer-filament and blackbody hole the eye might attribute the lower brightness of the region around the hole to the hole itself. Thus the hole brightness would be taken as an average of the brightness of the hole plus a small region about the hole. This would result in the measurement of the hole temperature being fictitiously lower than should be. Clearly this effect would disappear for a source of uniform brightness over a large area.

It might appear from this that measurement of temperatures of small filaments, etc., with an optical pyrometer would have some uncertainty unless the observer by comparison with several other observers or by other tests knows himself to be free of this defect.

<sup>4</sup> L. Malter and D. B. Langmuir, Phys. Rev. **55**, 743 (1939).

Values of  $\epsilon_{\lambda T}$  and  $T_B$  as function of  $T$  as taken from their graphs are given in Table I. Included are values listed by Malter and Langmuir,<sup>4</sup> by Utterbach and Sandermann,<sup>5</sup> and by Worthing.<sup>6</sup> It is seen that the various temperature scales are in fair agreement except at very high temperatures, and all show the same decrease in  $\epsilon_{\lambda T}$  with increasing  $T$ , in marked contrast with the temperature independent emissivities of other metals as found in this laboratory.<sup>7</sup>

### ELECTRON WORK FUNCTION

The experimental set-up and heat treatment schedule for measurement of the electron work function was that previously reported by Wahlin and co-workers.<sup>1</sup> A tantalum wire filament 0.070 cm in diameter was slightly flattened by rolling, bent into a hair pin shape, and mounted inside a collector plate equipped with a single guard ring. The slight flattening of the filament largely eliminated objectionable deviations from Lambert's law, so that the filament when heated appeared of uniform brightness across its entire width.

A careful schedule of baking, induction heating of collector plates, and heat treatment of the filament was followed for each specimen. At the end of a typical schedule of 300 hours with the filament at  $2600^\circ\text{K}$  a final vacuum of less than

TABLE I. Temperature scale and emissivity data for tantalum. W—Worthing; L-M—Langmuir-Malter; U-S—Utterbach-Sandermann.

$T$ °K	$T_B$ MDF-RWW	$T_B$ L-M	$T_B$ W	$T_B$ U-S	$\epsilon_{0.669}$		$\epsilon_{0.665}$ W
					MDF-RWW	L-M	
1250	1193				0.437	0.469	
1300	1238				.435		
1400	1327	1332	1329	1337	.430	.455	0.442
1500	1415				.425		
1600	1502	1508	1506	1508	.421	.442	.434
1700	1589				.416		
1800	1675	1682	1680	1678	.411	.431	.426
1900	1760				.406		
2000	1844	1851	1851	1843	.401	.421	.418
2100	1925			1926	.397		
2200	2007	2018	2018		.392	.413	.411
2300	2089				.388		
2400	2169	2181	2180		.384	.405	.404
2500	2249				.381		
2600	2329	2341	2339		.378	.399	.397
2700	2410				.375		
2800	2488	2499	2495		.372	.393	.390
2900	2561				.370		
3000	2634	2652	2647		.367	.388	.384
3100	2707				.365		
3200	2781	2803			.363	.384	
3300	2855		2870		.360	.381	.375

<sup>5</sup> C. L. Utterback and L. A. Sandermann, Phys. Rev. **39**, 1008 (1932).

<sup>6</sup> A. G. Worthing, Phys. Rev. **28**, 190 (1926).

<sup>7</sup> These include W, Mo, Fe, Ni, Co, Rh, Th, Pt, Cb.

$3 \times 10^{-8}$  mm of mercury was obtained for the entire temperature range employed.

Data were taken on three filaments on each of which an average of seven runs was made scattered over 200 hours. A Richardson plot for three runs scattered over 100 hours is shown in Fig. 2. The average deviation of experimental points from any of these linear plots covering a  $300^\circ$  range was less than  $0.5^\circ$ .

The Schottky correction to the work function owing to the field applied to insure absence of space-charge saturation was in each case less than 0.02 ev. This correction used with the value calculated from the Richardson plots leads to a work function of tantalum  $\varphi_0^- = 4.19$  ev with an average deviation of 0.02 ev, and an emission constant  $A^* = 55$  amp.  $\text{cm}^{-2}$   $\text{deg}^{-2}$  with an average deviation of 5 amp.  $\text{cm}^{-2}$   $\text{deg}^{-2}$ .

If one accepts with Riemann<sup>8</sup> a temperature dependence of the work function owing to thermal expansion of the lattice, one may readily show that the Richardson plot will yield the emission constant  $A$  as

$$A = A_1 \exp \left[ \frac{h^2 \alpha}{4mk} (3n/\pi)^{\frac{2}{3}} \right],$$

where  $h$ ,  $m$ ,  $k$  have their usual significance,  $n$  is the number density of free electrons,  $\alpha$  is the coefficient of linear expansion, and  $A_1 = 120$  amp.  $\text{cm}^{-2}$   $\text{deg}^{-2}$ . Employing Worthing's<sup>6</sup> value for  $\alpha$  one obtains for tantalum the theoretical emission constant  $A = 55.8$  amp.  $\text{cm}^{-2}$   $\text{deg}^{-2}$ . If the agreement of this with the experimental value is more than "purely accidental" as Wigner<sup>9</sup> would suggest, one would conclude that for tantalum as for most other pure metals the reflection coefficient is negligible, and moreover, that the roughness factor is unity. The latter conclusion is supported by the fact that filaments removed after use in the measurements exhibited specular reflection, had a very high polish, and felt slippery—characteristics of a microscopically smooth surface.

Table II presents a summary of the data on emission constants of tantalum. Cardwell's photoelectric determination of the work function is probably the best of the previous measures, for the others were obtained before the importance of vacuum conditions was understood.

<sup>8</sup> A. L. Riemann, *Nature* **133**, 833 (1934).

<sup>9</sup> E. Wigner, *Phys. Rev.* **49**, 696 (1936).

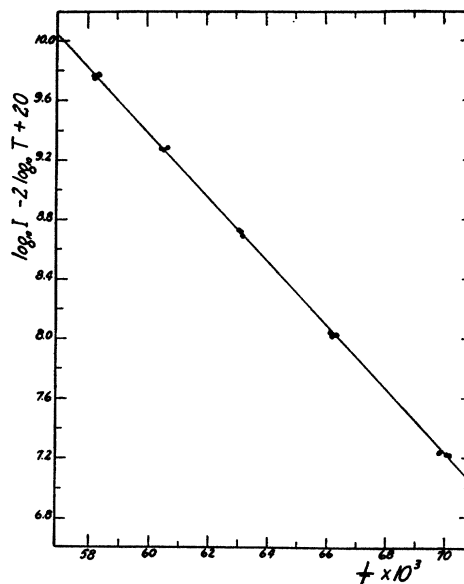


FIG. 2. Richardson electron plots for three different runs spread over 100 hours:  $\varphi_0^- = 4.19$  ev.  $A^* = 52$  amp.  $\text{cm}^{-2}$   $\text{deg}^{-2}$ .

Dushman used Worthing's temperature scale to obtain his thermionic values. His data plotted on the temperature scale of this work yield  $\varphi_0^- = 4.17$  ev,  $A^* = 85$  amp.  $\text{cm}^{-2}$   $\text{deg}^{-2}$  in good agreement with the values obtained here.

#### POSITIVE ION WORK FUNCTION

That metals raised to sufficiently high temperatures emit singly charged positive ions of the parent metal itself was first shown conclusively by Wahlin<sup>10</sup> and shortly after by Smith.<sup>11</sup> These emission currents in general were smaller than the electron emission currents at the same temperature by a factor of  $10^6$  or so and were appreciable only when there was considerable vaporization of the filament material.

Smith<sup>12</sup> applied Bridgman's<sup>13</sup> thermodynamic treatment of electron emission to this thermal emission of positive ions and obtained the equation

$$\ln I = -(\varphi_0^+ e/kT) + 2 \ln T + \ln 2\pi k^2 eM/h^3 + \ln(1-r) - (H/k) + S. \quad (1)$$

Here  $\varphi_0^+$  is the positive ion work function,  $M$

<sup>10</sup> H. B. Wahlin, *Phys. Rev.* **34**, 164 (1929).

<sup>11</sup> L. P. Smith, *Phys. Rev.* **34**, 1496 (1929).

<sup>12</sup> L. P. Smith, *Phys. Rev.* **35**, 381 (1930).

<sup>13</sup> P. W. Bridgman, *Phys. Rev.* **27**, 173 (1926).

the atomic mass;  $e$ ,  $k$ ,  $h$ , and  $T$  have the usual meaning;

$$H = \int_0^T \frac{dT}{T^2} \int_0^T C_{pm} dT, \quad (2)$$

in which  $C_{pm}$  is the specific heat at constant pressure of the ion in the metallic phase, and

$$S = \frac{S_p}{k} + \frac{1}{k} \int_0^T \frac{dT}{T^2} \int_0^T C_{pp} dT. \quad (3)$$

$C_{pp}$  is the specific heat at constant pressure associated with surface charging, and  $S_p$  is the entropy at  $T=0$  associated with the heat of surface charge.

$H$  may be evaluated by using the scheme of Jones, Langmuir, and Mackay.<sup>14</sup> For  $C_{pm}$  one uses  $C_{vm}$ , the specific heat at constant volume, in the temperature range  $0^\circ\text{K}$  to  $T_0^\circ\text{K}$  corrected with the semi-empirical equation of Lindemann and Magnus<sup>15</sup>  $C_{pm} = C_{vm} + aT^{\frac{1}{2}}$ .  $a$  is a constant calculated from a similar thermodynamic relation

$$C_{pm} = C_{vm} + (9\alpha^2 V / \beta T^{\frac{1}{2}}) T^{\frac{3}{2}},$$

where  $V$  is the atomic volume, and  $\alpha$  is the coefficient of linear expansion and  $\beta$  the compressibility both for the metal at the temperature  $T$ .  $C_{vm}$  is obtained directly from the Debye theory of specific heats in terms of  $\theta$ , the characteristic temperature of the metal.

This value of  $C_{pm}$  is plotted from  $0^\circ\text{K}$  to a temperature  $T_0$  where the plot intersects a

TABLE II. Emission constants for tantalum.

Observer	Date	$A^*$ amp cm <sup>-2</sup> deg. <sup>-2</sup>	$\varphi_0^-$ ev
I. Langmuir <sup>1</sup>	1913	30	4.0
I. Langmuir <sup>2</sup>	1916	28	4.05
H. Lester <sup>3</sup>	1916		4.44†
H. J. Spanner <sup>4</sup>	1924		4.2
S. Dushman <sup>5</sup>	1925	60	4.12
Cardwell <sup>6</sup>	1931		4.12-4.19*
Rentschler <sup>7</sup>	1932		4.12*
Fiske	1941	55	4.19

\* Photoelectric.

† Calorimetric.

Unmarked are thermionic.

<sup>1</sup> Phys. Rev. **2**, 450 (1913).

<sup>2</sup> Trans. Am. Electrochem. Soc.

**29**, 125 (1916).

<sup>3</sup> Phil. Mag. **31**, 197 (1916).

<sup>4</sup> Ann. d. Physik **75**, 609 (1924).

<sup>5</sup> Phys. Rev. **25**, 338 (1925).

<sup>6</sup> Phys. Rev. **38**, 2041 (1931).

<sup>7</sup> Rev. Sci. Inst. **3**, 794 (1932).

<sup>14</sup> Jones, Langmuir, and Mackay, Phys. Rev. **30**, 201 (1927).

<sup>15</sup> F. A. Lindemann and A. Magnus, Zeits. f. Electrochem. **16**, 269 (1910).

straight line drawn through the experimental high-temperature values of  $C_{pm}$ , which may be represented by  $C_{pm} = N + ZT$ .

One then obtains for  $H$

$$H = N \ln T + \frac{Z}{2} T + \frac{1}{T} \left( NT_0 + \frac{ZT_0^2}{2} - E(T_0) - \frac{2}{5} a T_0^{5/2} \right) - N \ln T_0 - ZT_0 + F(T_0) + \frac{4}{15} a T_0^{3/2} + \frac{1}{T_0} E(T_0) + \frac{2}{5} a T_0^{3/2}. \quad (4)$$

Here

$$E(T_0) = \int_0^{T_0} C_{vm} dT$$

and

$$F(T_0) = \int_0^{T_0} \frac{dT}{T^2} \int_0^T C_{vm} dT$$

are given in *Handbuch der Physik*<sup>16</sup> as  $E/T$  and  $F/T$ , functions of  $\theta/T$ .

The only data on the specific heat of tantalum are those of Pirani<sup>17</sup> obtained in 1912. His data show such a spread for the few points taken that the uncertainty in  $N$  and  $Z$  is very great. Further, the purity of the tantalum prepared at this early date is rather questionable. The best values for the data seem to be  $N = 5.35$  cal. g-atom<sup>-1</sup> deg.<sup>-1</sup> and  $Z = 15 \times 10^{-4}$  cal. g-atom<sup>-1</sup> deg.<sup>-2</sup>.

Seitz<sup>18</sup> lists  $\theta$  for tantalum as  $245^\circ\text{K}$ .  $a$  may be computed to be  $a = 1.18 \times 10^{-5}$  cal. g-atom<sup>-1</sup> deg.<sup>-5/2</sup>, whence

$$H = -32.0 + 12.32 \log_{10} T + 7.5 \times 10^{-4} T + 2530/T. \quad (5)$$

Then the positive ion equation becomes

$$\log_{10} I + 0.688 \log_{10} T + 1.64 \times 10^{-4} T + 554/T = -5032 \varphi_0^+ / T + F, \quad (6)$$

where

$$F = S/2.303 + \log_{10} (1-r) + 14.29. \quad (7)$$

The experimental arrangement and procedure for measurement of the positive ion emission

<sup>16</sup> *Handbuch der Physik* (Julius Springer, Berlin, 1910), Vol. 10, p. 368.

<sup>17</sup> M. Pirani, Verh. d. Phys. Ges. **14**, 1037 (1912).

<sup>18</sup> F. Seitz, *Modern Theory of Solids* (McGraw-Hill, 1940), Chapter 3.

from tantalum were the same as for electron emission, except that the collecting potential was reversed. Positive ion runs were usually taken immediately preceding or following an electron run. The emission current was measured as a function of  $T$  and the left side of (6) plotted as a function of  $1/T$ . The slope of this line had the value  $5032 \varphi_0^+$  ev and the intercept had the value  $F^*$ . Figure 3 shows such a plot.

Some 22 different runs were taken on the three filaments. The data obtained showed a much lower reproducibility and greater day-to-day variation than did the electron data. Consecutive runs occasionally differed by half a volt or so in  $\varphi_0^+$  while  $F^*$  shifted 1.0 to 1.5 or so, although  $\varphi_0^-$  would be constant to 0.01 ev and  $A^*$  be virtually unchanged. No consistent variation of  $\varphi_0^+$  and  $F^*$  could be found with varying conditions. Previous filament temperature history, vacuum conditions, procedures in a run, etc., were all changed, but no significant drift of the positive ion emission followed them. Average deviation of points from the linear plot was  $2^\circ$ , four times that for the electron plots. Thus it is felt that this work cannot assign  $\varphi_0^+$  closer than 0.3 ev to the average  $\varphi_0^+ = 10.0$  ev.  $F^*$  is uncertain to 1.0 about 13.0.

From (7) and  $F^*$  the measured value of  $F$  we must have

$$13.0 = 14.29 + \log_{10}(1-r) + (S/2.303).$$

If we tentatively disregard  $S$  we see that  $\log_{10}(1-r) = -1.29$ , or  $r = 0.94$ , and all but 6 percent of the ions approaching the surface are reflected. This is greatly in contrast with the case for electrons or neutral atoms for which  $r$  is about zero. On the other hand if we disregard  $r$ , then  $S$  is not negligible, and there is an appreciable contribution to  $F$  from the heat of surface charge. One notes that this would demand that any temperature variation of the second term of (3) be assigned to other terms in the positive ion equation, and this must eventually be borne by  $\varphi_0^+$ .

#### THERMATOMIC WORK FUNCTION

A metal heated to temperatures approaching its melting point vaporizes at such an appreciable rate that its rate of mass loss per unit area  $m$ , may be measured as a function of temperature.

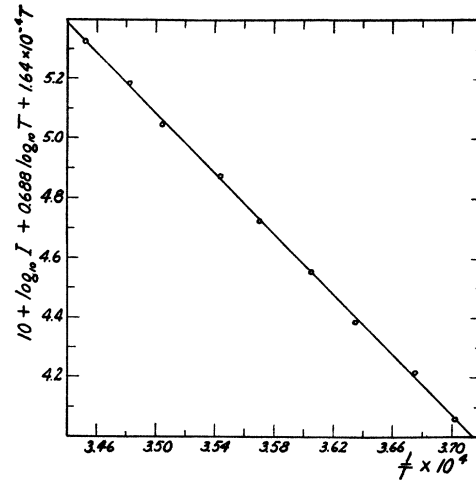


FIG. 3. Richardson positive ion plot  $\varphi_0^+ = 10.10$  ev.  $F^* = 13.05$ .

The metallic vapor obeys ideal gas laws and hence the equilibrium state between the metal and its vapor may be treated in a simple thermodynamical way to obtain the vapor pressure  $p$  as a function of temperature. Kinetic theory reasoning serves to connect  $m$  with  $p$ .

Jones, Langmuir, and Mackay<sup>14</sup> employed this line of reasoning to obtain a measure of  $L_0$ , the latent heat of vaporization at the absolute zero:

$$L_0/T = 4.577(2 \log_{10} M + 2 \log_{10} T + 0.058 - \log_{10} m) - H.$$

If one uses for  $H$  the expression (5) he obtains for tantalum

$$(5032/T) \varphi_0^0 = 53.0 - 3.17 \log_{10} T - 4.577 \log_{10} m - 7.5 \times 10^{-4} T - 2530/T.$$

Here the writer has used  $\varphi_0^0$ , the thermatomic work function,<sup>19</sup> as a terminology more consistent with "positive ion work function" and "electron work function" than is the more cumbersome "latent heat of vaporization."

$m$  is usually measured by one of two methods. The first is to follow the change in radius of a cylindrical filament in vacuum by following its change in resistance which varies inversely as the square root of the radius providing the resistivity remains constant. This method is subject to a

<sup>19</sup> This phrase was suggested to the writer by Professor H. B. Wahlin.

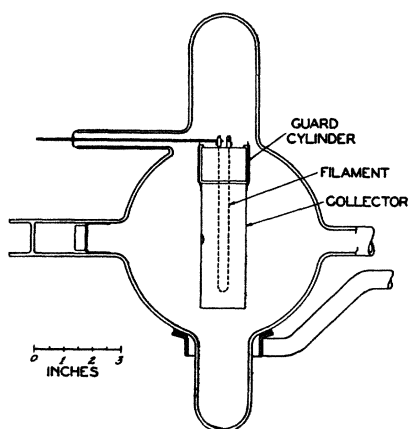


FIG. 4. Tube for evaporation data.

systematic error due to a change in resistivity caused by outgassing and recrystallization. Malter and Langmuir<sup>20</sup> found an apparent change in resistivity of 0.2 percent for a tantalum wire during an evaporation run. This corresponded roughly to a 2.5 percent error in mass loss determination.

The other method consists of actually weighing the filament to determine its mass loss. The procedure usually is to operate two identical filaments under identical preliminary outgassing and heat-treatment conditions. Then one alone is raised to an elevated temperature for a definite time. The mass difference between equal lengths from the two filaments will then give the desired mass loss. This procedure is also subject to serious errors. In order to avoid development of "hot spots" it is necessary to evaporate as little as can be accurately weighed. Yet in cutting and handling the filament and measuring its length it is difficult to eliminate errors which are an appreciable fraction of the mass loss itself.

In view of these difficulties a different method for measuring was tried. The filament was entirely surrounded by a 0.001-inch thick tantalum collector cylinder so that upon this cylinder would deposit all the metal evaporated from the filament within. This collector was hooked over a guard cylinder provided above (see Fig. 4) to make the filament within the collector all at the same temperature. The filament was pyrometered through a small hole in the side of the collector.

<sup>20</sup> D. B. Langmuir and L. Malter, *Phys. Rev.* **55**, 748 (1939).

The technique of measuring  $m$  was to operate the filament during preliminary baking and outgassing at a temperature where evaporation was inappreciable (1600°K), then to raise it to the evaporation temperature for a definite time—20 minutes to several hours—and then to remove the collector cylinder and measure on a microbalance its gain in mass. The collector was handled entirely by tools and carefully protected from dust.<sup>21</sup>

The results of seven runs are shown in Table III. Also included in this table are the data of Langmuir and Malter after conversion to the temperature scale used in this work. The data are insufficient to permit use of a Richardson type plot for an experimentally more significant evaluation of  $\varphi_0^0$ . The mean deviation from the average value of 7.97 eV is 0.03 eV, certainly less than the probable error of the determination.

Examination of the method indicates that the only serious source of error lies in run-to-run variation of air contamination of the collector when it is removed from the vacuum system. This is rather difficult to evaluate. Humidity variation is the most serious contributor to this error. However, simple tests indicated that the error is under 5 percent, and prompt weighing of the collector after removal reduces this to the order of 1 percent.

Air contamination may be eliminated entirely by use of a magnetically operated balance enclosed within the vacuum system, as described by Blewett.<sup>22</sup> This device was tried, but the desired sensitivity and reproducibility could not be obtained and use of such a balance was discarded.

#### IONIZATION POTENTIAL

There appears nowhere in the literature a value of the ionization potential of tantalum and apparently there are no sufficiently high term values to permit a spectroscopic estimation of it. In a private communication Dr. C. C. Kiess of the National Bureau of Standards estimated that for tantalum  $V=7.3$  eV. He based his estimate on an interpolation from neighboring elements in the periodic table.

<sup>21</sup> Changes in mass of the 10-gram collector of the order of 5 milligrams could be reproducibly measured to 20 micrograms.

<sup>22</sup> J. P. Blewett, *Rev. Sci. Inst.* **10**, 231 (1939).

The writer estimates from an interpolation in group V of the periodic table that  $V=7.4$  ev while an interpolation of Series 10 leads to  $V=7.3$  ev. The uncertainty in such interpolation must be at least 0.3 ev.

#### THE ENERGY CYCLE

Collecting the foregoing determined values of the terms involved in the energy cycle we find  $\varphi_0^- = 4.19 \pm 0.02$  ev;  $\varphi_0^+ = 10.0 \pm 0.3$  ev;  $\varphi_0^0 = 7.97 \pm 0.05$  ev; and  $V = 7.3 \pm 0.3$  ev. Then  $\varphi_0^- + \varphi_0^+ = 14.2 \pm 0.3$  ev and  $\varphi_0^0 + V = 15.3 \pm 0.4$  ev. The probable values fail to close the cycle by 1.1 ev, and even for the limit values there is still lacking 0.4 ev.

Several possibilities present themselves as reasons for the energy cycle not closing. The evaporation of a neutral atom from a lattice is not a simple process. One may visualize it as concurrent evaporation of an electron and a positive ion with recombination in close proximity of the surface. It seems not unlikely that in the recombination lattice vibrations are set up which introduce into the cycle an irreversible term of magnitude difficult to estimate.

The fact that the electron work function is measured at temperatures  $1200^\circ$  below those at which the positive ion work function is determined suggests that the emitting surface itself may be different. If there exists a high-temperature Curie point so that the body-centered lattice shifts to, for instance, a face-centered lattice the cycle certainly would fail to close by

the difference of the work functions from these different structures.

The factors determining the statistical distribution of exposed crystal faces in the thermionic surface are not as yet understood, and one cannot overlook the possibility that this distribution is temperature dependent. This most certainly would introduce a temperature-dependent measured work function. Such a variation even if small in the ordinary range of thermionic measures would become appreciable over the temperature interval separating measurement

TABLE III. Evaporation data of tantalum.

$T^\circ\text{K}$	$\frac{m}{\text{g cm}^{-2} \text{sec.}^{-1}}$	Langmuir-Malter $\frac{m}{\text{g cm}^{-2} \text{sec.}^{-1}}$	$\varphi_0^\circ$ ev
2633	$2.88 \times 10^{-7}$	$0.693 \times 10^{-7}$	7.90
2649	2.80	0.867	7.95
2700	4.38	1.66	7.98
2737	6.59	2.61	7.99
2804	16.0	5.80	7.96
2807	12.4	6.04	8.04
2850	23.0	9.87	8.02

ranges of the two work functions. Hence again the energy cycle even if exact at any single temperature would seem not to be closed when applied to widely different surface conditions at greatly separated temperatures.

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