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THE EMISSION OF POSITIVE IONS FROM TUNGSTEN AND MOLYBDENUM

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Abstract

An examination of the positive ion emission from tungsten and molybdenum has been made in which it was sought to determine the following points: (1) The nature of the ions emitted at various temperatures; (2) the temperature variation of the positive ion current; (3) the theory of positive ion emission with regard to where and how the ions are formed; (4) the positive ion work function for these metals; (5) whether the work function, determined by experiment, checks with that calculated by a simple cyclic process involving the thermionic work function, the ionizing potential, and the latent heat of evaporation of the metal.

The mass spectrum for tungsten and molybdenum filaments taken at moderate temperatures (1700° to 2000°K) has shown that the emitted ions consist of sodium, the two isotopes of potassium, and aluminum. At high temperatures these impurities disappear and finally both tungsten and molybdenum filaments yield positive ions of their own metal. The latter confirm a report by Wahlin. The temperature variation of the positive ion current at high temperature yields a value of 6.55 volts for the positive ion work function of tungsten and 6.09 volts for that of molybdenum. These values disagree widely from the values 10.88 volts and 9.26 volts calculated from the simple cyclic process mentioned above. This suggests that the ions are formed as a by-product of an irreversible recrystallization of the metal. Theoretical considerations show that the ions are emitted from the metal and are not formed after a neutral atom evaporates.

UNTIL recently, it has been thought that any positive ion emission from metals was due entirely to ionized atoms of one or more impurities which existed in the metal. O. W. Richardson[1] has shown that most metals contain a very small amount of potassium which is driven out of the metal as the temperature is raised. He obtained rather erratic results from tungsten and did not give any data concerning molybdenum. His work was carried on for temperatures below 2,000°K. J. J. Thomson[2] investigated the positive ion emission from platinum by crossed electric and magnetic fields and found in addition to those of alkaline impurities, ions having an atomic weight of 27 which he concluded were ionized CO molecules. More recent work[3] has shown definitely that platinum contains potassium and sodium as impurities which are ionized and emitted at high temperatures.

During the summer of 1927 the author attempted to perfect a pliotron having a grid extremely well insulated. It was found during the course of this investigation that part of the electric leakage to the grid was due to positive

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[1] O. W. Richardson. Emission of Electricity From Hot Bodies.

[2] J. J. Thomson, Camb. Phil. Proc. **15,** 64 (1908).

[3] Barton, Harnwell, and Kunsman, Phys. Rev. **27,** 739 (1926).

ions arising at the filament. These ions persisted even after the filament was flashed to some 3,000° and then well aged. An investigation of the nature of these high temperature ions and the variation of the positive ion current with temperature was undertaken. After the work was begun it was noted that Jenkins[4] had found that the tungsten cathode of a Coolidge x-ray tube was a source of positive ions. Mitra[5] carried on the investigation and obtained data on the temperature variation of the positive ion current using a commercial type of radio tube having a tungsten filament, but did not attempt to determine the positive ion work function. The author has given a preliminary report[6] on such a work function.

Mass Spectrograph

The apparatus for obtaining the mass spectrum of the ions is shown diagrammatically in Fig. 1. It consisted essentially of a copper tube A in the form of a half torus ring spun from sheet copper. The diameter of the cross section was approximately 2.5 cm. Caps having the slits S_1 and S_2 were placed over the ends. The slit S_1 was about 0.8 mm wide and 8 mm long. The slit S_2 was somewhat larger being about 3 mm wide and 1 cm long. A wire filament of the metal under investigation having a length of about 1.4 cm was placed at F, parallel to the slit S_1 and about 5 mm away from it. Ions passing through S_1 and bent by the magnetic field on an arc whose radius was 6.95 cm were focused at S_2. Those passing through S_2 were collected on the electrode C which was connected to a quadrant electrometer. The accelerating potential was applied between D and F. The copper tube together with the filament leads and collector leads were all sealed into a glass tube B which was exhausted at E. A pressure less than 10^{-6} cm of Hg was maintained. The tube was placed between poles of an electromagnet having pole pieces of large diameter. The field in the region occupied by the tube was found to be uniform and its intensity was determined by careful flip coil measurements.

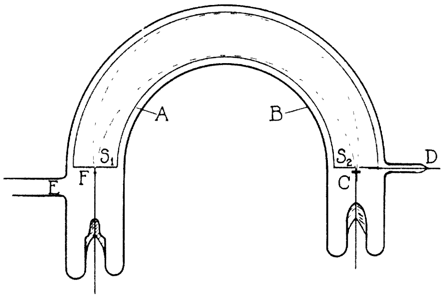

Fig. 1. Diagram of mass spectrograph.

In determining the mass spectrum, the field intensity was set at a given value and the accelerating potential was varied very slowly but continuously

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[4] Jenkins, Phil. Mag. **47,** 1025 (1924).

[5] Mitra, Phil. Mag. **5,** 67 (1928).

[6] Smith, Phys. Rev. **33,** 279 (1929).

by a mechanical device. The presence of a particular ion was noted by a drift of the electrometer. When it began to drift, the rate of drift for various accelerating potentials was taken and from these data the voltage yielding the maximum rate of drift was obtained. The voltage across the filament was measured and one half of this drop was added to the voltage producing maximum drift to yield the true accelerating potential.

Nature of the Ions

From the accelerating potential corresponding to a given electrometer current, the atomic weight W was computed by means of the expression $W=(1/V)\ [RH/144.5]^2$ where R is the radius of the path traversed in cm, H is the field intensity in gauss, and V is the accelerating potential in volts. The electrometer current in arbitrary units was plotted against W to give a mass spectrogram. A typical mass spectrum for tungsten at moderate temperature is shown in Fig. 2. The peak at $W=23.1$ is due to sodium ($W=23.0$) and could be detected at a temperature of about 1700°. The peaks at $W=39$ and 41.1 were also present at this temperature. They are undoubtedly due to the two isotopes of potassium occurring at $W=39$ and 41. The only element falling in this region is calcium($W=40.07$). No evidence of calcium ions has been found and in fact it would be quite improbable that any appreciable amount of calcium would be ionized at these temperatures for its ionization potential is too high (6.09 volts). The peak occurring at $W=27.2$ did not show up until temperatures over about 2,000° were reached. This atomic weight compares well with aluminum ($W=27.0$), and since the ionizing potential of aluminum is 5.9 volts we would not expect to find it until a higher temperature is reached than would yield either potassium or sodium ions whose ionizing potentials are 4.3 and 5.1 volts respectively. As mentioned before, J. J. Thomson found ions of atomic weight 27 emitted from platinum and concluded that they were ions of CO molecules ($W=28$). It seems improbable that these were really positively ionized CO molecules because the ionizing potential of such molecules is of the order of 14 volts, much too high to have any ions of CO present

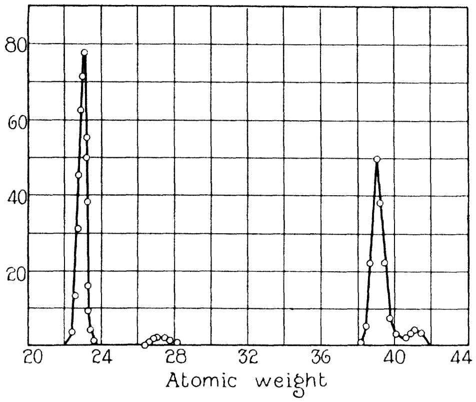

Fig. 2. Mass spectrum from tungsten at moderate temperatures (1600–2000°K).

below the melting point of platinum. It therefore seems extremely likely that aluminum was present as an impurity.

Fig. 3 is the mass spectrum obtained from molybdenum. It shows the presence of the same impurities as existed in the tungsten. This spectrum does not show as high a resolution as the one for tungsten but this is doubtless due to the fact that it was obtained at a higher temperature and the voltage drop along the filament broadened the peaks. It is interesting to note that these impurities are present in extremely small amouts. A spectroscopic analysis was made on the samples of tungsten and no trace of the impurities here detected was found, which indicates that each was probably present in an amount less than 1 part in 100,000 and certainly less than 1 part in 10,000.

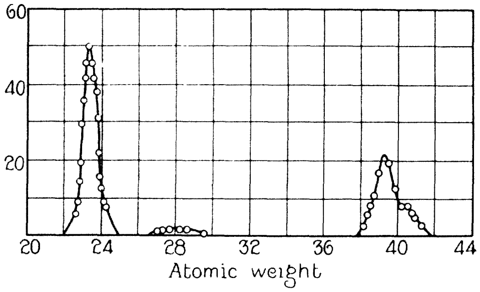

Fig. 3. Mass spectrum from molybdenum at moderate temperatures.

These ions which are emitted at moderate temperatures become less in number as time of heating increases and they can be gotten rid of quite rapidly if the filament is aged at higher temperatures. As the temperature is increased a point is found where no ions of impurities are emitted. On further increasing the temperature to about 2500° for tungsten and 2300° for molybdenum new ions are emitted. The spectrum curves for molybdenum and tungsten at these temperatures are plotted in Fig. 4. These spectra leave no doubt that the high temperature ions from tungsten found by Jenkins and the author are really tungsten ions, and that molybdenum also emits positive ions

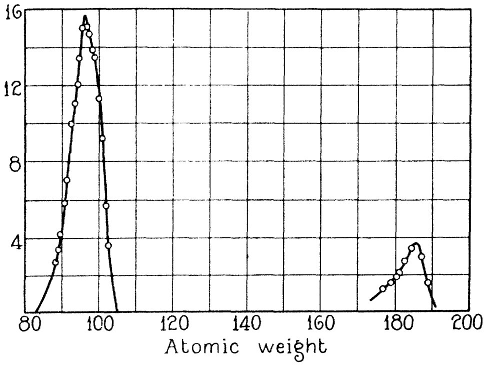

Fig. 4. Mass spectrum of molybdenum and tungsten at high temperatures.

of molybdenum. While this paper was being prepared Wahlin reported in a brief note[7] that he had found tungsten, molybdenum, tantalum, and rhodium to emit positive ions of their own metal. The results given here corroborate his results for tungsten and molybdenum.

No trace of doubly ionized atoms was found nor was there any evidence of ions which were singly charged but having a mass of two or more atoms of the material, although they were looked for. It appears that the ion of the metal is emitted as a singly ionized atom.

VARIATION OF EMISSION WITH TEMPERATURE

To obtain the magnitude of the positive ion current for a given temperature, the form of tube shown in Fig. 5 was used. The current to the lower cylinder was measured. For tungsten, the temperature was determined from the current through a given sized filament as given by Langmuir and Jones.[8] For molybdenum the temperature was determined from data kindly supplied by S. Dushman giving the watts per cm^2 as a function of the temperature. Volt-ampere characteristics of two hair pin filaments were taken. They had the same diameter but different lengths, and were electrically welded to identical lead wires. By a method of differences the cooling effect of the leads was eliminated and the temperature of the center of the longer filament was obtained as a function of the current through it.

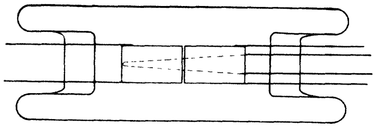

Fig. 5. Tube used to measure the positive ion current.

The magnitude of the positive ion current from tungsten at a given temperature depends on the heat treatment through which the filament has passed. Furthermore there exists a decay with time which is slow after the filament has been allowed to age for a time and has been carried over the range

TABLE I. *Variation of positive ion current with temperature.*

Tungsten		Molybdenum	
Current per cm^2	Temp. °K	Current per cm^2	Temp. °K
5.39×10^9	2390	2.43×10^9	2300
9.71	2450	3.89	2340
18.3	2500	5.71	2375
25.1	2560	7.79	2400
62.6	2585	9.71	2420
79.2	2635	13.6	2460
113.	2670	17.3	2470
168.	2715	20.4	2490
276.	2760	24.3	2500
424.	2800	29.1	2520

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[7] Wahlin, Phys. Rev. **34,** 164 (1929).

[8] Langmuir and Jones, General Electric Rev. p. 510, June 1927.

of temperatures to be used. Hence in the case of tungsten no final value of the current at a given temperature can be given. After a few hours aging at about 2300°, molybdenum seemed to give values that were reproducible. These values could be duplicated after aging for several hours more at 2300°. Table I shows data for tungsten and molybdenum obtained after some 5 hours aging.

POSITIVE ION "WORK FUNCTION"

In determining electronic work functions it has been customary to make use of the usual electron emission formula

$$I = AT^2\epsilon^{-(\phi_-e/kT)}.$$

The work function ϕ_- is found by plotting $\log I - 2\log T$ against $1/T$ and determining the slope of the straight line thus found. This procedure however would be incorrect for determining the work function for positive ions because of the difference in the process involved in the evaporation of ions. We shall therefore deduce an expression which should be applicable for the evaporation of ions.

Following Bridgman[9] we take a neutral metal composed of n atoms at 0° absolute and raise its temperature to T and evaporate m ions reversibly at the equilibrium pressure. At this temperature we then have a positive ion gas, a negative surface charge, and the remaining neutral metal. Let the entropy of one atom in the condensed state be denoted by s_1, the entropy of one evaporated ion by s_2 and the entropy to be associated with the heat of surface charging produced by the evaporation of one ion by s_2'. The entropy before evaporation is then ns_1 and the entropy after the evaporation of m ions is $ms_2 + ms_2' + (n-m)s_1$. Since the entropy after evaporation minus the enentropy before evaporation must equal the change of entropy during evaporation we have,

$$(mL/T) = m(s_2 + s_2') + (n-m)s_1 - ns_1$$

where L is the latent heat of evaporation of one ion, the metal being isolated. This expression reduces to

$$(L/T) = s_2 + s_2' - s_1. \tag{1}$$

Using essentially the same expressions for s_1, s_2 and s_2' as Bridgman, Eq. (1) becomes—

$$\begin{aligned}\frac{L}{T} = k\left[\frac{5}{2} + \log_\epsilon \frac{(2\pi M)^{3/2}k^{5/2}}{h^3} + \frac{5}{2}\log_\epsilon T - \log_\epsilon P\right] \\ + \int_0^T \frac{C_{p\rho}}{T}dT - \int_0^T \frac{C_{pm}}{T}dT + s_\rho\end{aligned} \tag{2}$$

where p is the equilibrium vapor pressure of the ion gas; M is the mass of one ion; C_{pm} is the heat capacity, at constant pressure, of an ion in the condensed

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[9] Bridgman, Phys. Rev. **27**, 173 (1926).

state; $C_{p\rho}$ is the heat capacity associated with the surface heat of charging produced by the evaporation of one ion, and s_ρ is the entropy associated with the surface heat of charging at $T=0$.

The latent heat of evaporation may be expressed as a function of the temperature by the relation[9]

$$L_T = L_0 + (5/2)\ kT + \int_0^T C_{p_\rho} dT - \int_0^T C_{pm}\ dT \tag{3}$$

Combining Eqs. (2) and (3) we have:

$$\log_\epsilon p = -\frac{L_0}{kT} + \frac{5}{2}\log_\epsilon T + \log_\epsilon \frac{(2\pi M)^{3/2}k^{5/2}}{h^3} + \frac{s_\rho}{k} + \frac{1}{k}\left[\int_0^T \frac{C_{p\rho}}{T}dT - \frac{1}{T}\int_0^T C_{p\rho}dT\right] - \frac{1}{k}\left[\int_0^T \frac{C_{pm}}{T}dT - \frac{1}{T}\int_0^T C_{pm}dT\right]$$

This reduces to

$$\log_\epsilon p = -\frac{L_0}{kT} + \frac{5}{2}\log_\epsilon T + \log_\epsilon \frac{(2\pi M)^{3/2}k^{5/2}}{h^3} + \frac{1}{k}\int_0^T \frac{dT}{T^2}\int_0^T C_{p\rho}dT + \frac{s_\rho}{k} - \frac{1}{k}\int_0^T \frac{dT}{T^2}\int_0^T C_{pm}dT. \tag{4}$$

Under equilibrium conditions just as many ions condense as are evaporated per second, hence we may take the rate at which ions strike the surface of the metal at the equilibrium pressure as the rate of evaporation. It may be shown that at the pressure p the number of ions striking unit area per sec is

$$n = p/(2\pi MkT)^{1/2}$$

where M is the mass of the atom concerned. If some of the ions striking the metal are not condensed but are reflected then the number emitted must be $n=(1-r)p/(2\pi MkT)^{1/2}$ where r is a reflection coefficient. The positive ion current will be given by

$$I = ne = \frac{pe(1-r)}{(2\pi MkT)^{1/2}}$$

or

$$\log_\epsilon p = \log I + \tfrac{1}{2}\log_\epsilon 2\pi MkT - \log_\epsilon e - \log(1-r). \tag{5}$$

Making use of (5), Eq. (4) becomes:

$$\log_\epsilon I = -\frac{L_0}{kT} + 2\log_\epsilon T + \log_\epsilon M + \log_\epsilon 2\pi k + \log_\epsilon \frac{k}{h^3} + \log_\epsilon e + \log_\epsilon(1-r) + \frac{1}{k}\int_0^T \frac{dT}{T^2}\int_0^T C_{p\rho}dT + \frac{s_\rho}{k} - \frac{1}{k}\int_0^T \frac{dT}{T^2}\int_0^T C_{pm}dT$$

or

$$\log_\epsilon I = -\frac{L_0}{kT} + 2\log_\epsilon T + \log_\epsilon M + \log_\epsilon \frac{2\pi k^2 e}{h^3} + \log_\epsilon (1-r) + \frac{1}{k}\int_0^T \frac{dT}{T^2}\int_0^T C_{p\rho}dT + \frac{s_\rho}{k} - \frac{1}{k}\int_0^T \frac{dT}{T^2}\int_0^T C_{pm}dT. \tag{6}$$

The integral containing C_{pm} has been evaluated[10] for tungsten and molybdenum. Making use of the evaluation for tungsten and changing to logarithms to the base ten, Eq. (6) becomes

$$\log_{10} I + 0.363\log_{10} T + 1.64\times 10^{-4}T = \frac{-\phi_{+0}e}{2.203kT} + \frac{1}{2.303k}\int_0^T \frac{dT}{T^2}\int_0^T C_{p\rho}dT + \frac{s_\rho}{2.303k} + \log_{10}(1-r) + 12.43. \tag{7}$$

Where $\phi_{+0} = L_0/e$ is the equivalent difference of potential through which an ion must be moved. The corresponding equation for molybdenum is,

$$\log_{10} I + 0.453\log_{10} T + 2.70\times 10^{-4}T = \frac{-\phi_{+0}e}{2.303kT} + \frac{1}{2.303k}\int_0^T \frac{dT}{T^2}\int_0^T C_{p\rho}dT + \frac{s_\rho}{2.303k} + \log_{10}(1-r) + 12.76. \tag{8}$$

If it were known how $C_{p\rho}$ varied with the temperature then the above equation would show exactly how the positive ion current varies with the temperature and the work function ϕ_{+0} could be found by putting all functions of T on the left hand side of the equation except the term containing ϕ_{+0} and plotting it against $1/T$. The slope of the straight line so obtained would yield ϕ_{+0}.

Langmuir and Tonks[11] have shown that the surface heat of charging for the removal of electrons from a surface is very small i.e., of the order of 0.04 volts, at 2270°. Although the fact that it is small does not mean that it cannot vary rapidly with the temperature, we shall for the present assume $C_{p\rho} = 0$.

Fig. 6 shows the result of plotting the data for tungsten according to Eq. (7). Curve I is that obtained by plotting the data for tungsten given in Table I. The points lie very close to a straight line. Curve II was obtained after a sample of tungsten had aged some 30 hours and the rate of decay of the positive ion current had become very small. The point to be noticed is that even though a decay has taken place and the positive ion current has become smaller for a given temperature it has the same temperature variation as it had for considerably less aging, for the slopes of the lines I and II are the same. Curve III shows the result of plotting the data given by Mitra according to Eq. (7), As is evident, the curve so obtained has a slope almost identi-

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[10] Jones, Langmuir and Mackay, Phys. Rev. **30**, 201 (1927).

[11] Langmuir and Tonks, Phys. Rev. **29**, 524 (1927).

cal to that of Curves I and II. The fact that it is displaced relative to the other lines does not yield any definite information because the area of emission used by him was not given. Since the slopes of these curves are the same the work function ϕ_{+0} is definitely determined. Eq. (7) represents each of the Curves I and II with suitable change in the constant term. A discussion concerning the value of the constant term will be given later.

As stated before, molybdenum after suitable aging gave reproducible results. The data given for Mo in Table I were plotted according to Eq. (8). Fig. 7 shows how well these data give a straight line thus determining a value for ϕ_{+0} for Mo.

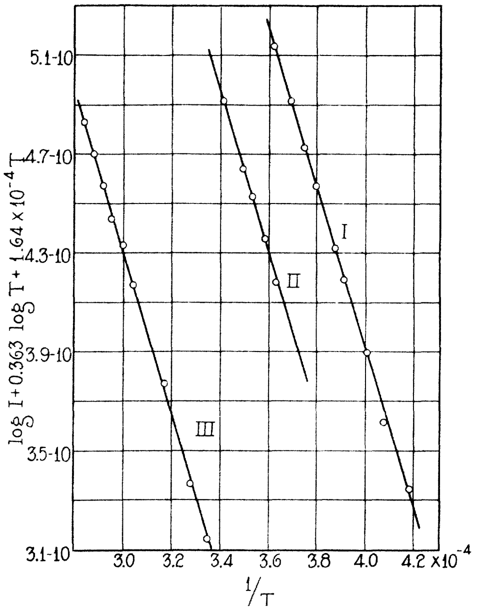

Fig. 6. Curves for determining the positive ion work function of tungsten.

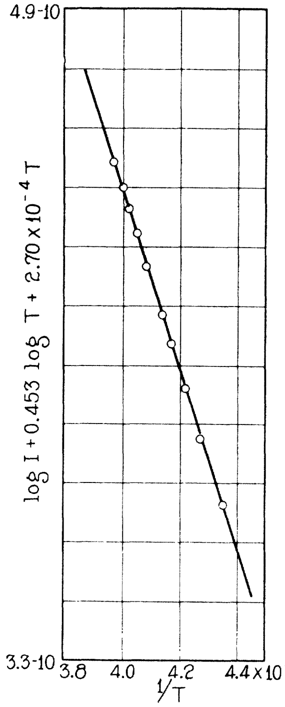

Fig. 7. Work function curve for molybdenum.

From Curve I, Fig. 6, ϕ_{+0} for tungsten is 6.55 volts, ϕ_{+0} determined from Curve II is 6.60 volts and from Mitra's data $\phi_{+0} = 6.55$ volts. It cannot be inferred that ϕ_{+0} is determined with an accuracy suggested by these figures for a slightly different line through the points yields a considerably different ϕ_{+0} as regards the third place, but 6.55 volts is undoubtedly a good representative value. The curve for molybdenum gives $\phi_{+0} = 6.09$ volts.

The constant term that must appear in Eq. (7) to represent the data plotted in Curve I, Fig. 6, is 6.51. If Curve II is considered to have the same slope as Curve I then the constant term for it is 6.28. From the curve for Mo it is found that the constant term of Eq. (8) must be 6.90.

Two serious difficulties now present themselves. The first is in regard to the constant terms just determined. Each of them is respectively much smaller than the numerical term appearing on the right side of Eqs. (7) and (8). On the assumption that the entropy associated with the surface heat of charging is zero, the constant 12.43 in Eq. (7) must be reduced to the value obtained (about 6.5) solely by the magnitude of the reflection coefficient r. To yield the proper constant, r would have to be so great that only 1 ion out of about 100,000 striking unit area would be condensed. It appears, however, that there is no quantitative evidence for such high values of r. For the evaporation of atoms, it has been found that satisfactory results are obtained when r has been assumed to be equal to or nearly zero, and even in thermionic emission r is probably not greater in order of magnitude than 0.5. Even if it had not been assumed that the entropy associated with the surface charge was zero, it is not likely that it would contribute a negative entropy constant term in Eqs. (7) and (8). Such a negative entropy would mean that heat would be developed when the metal surface became negatively charged and seems improbable. In fact evidence is presented later to indicate that heat is absorbed in the process of charging a metallic surface negatively.

The second difficulty seems more serious than the first. If we consider an inclosure in which molybdenum say is in equilibrium with its radiation at a given temperature T we may carry out the following cycle. Remove an electron and positive ion from the metal thus requiring an amount of work $\phi_{-T}+\phi_{+T}$ where ϕ_{-T} and ϕ_{+T} are the respective work functions at the temperature T, then allow the electron and ion to recombine thus producing a neutral atom and yielding an amount of energy corresponding to its ionizing potential V. Then let the atom condense on the metal thus yielding the heat of condensation. This is a reversible cycle and the sum of all the energy transfers should vanish thus:

$$\phi_{+T}+\phi_{-T}=V+U_T \tag{9}$$

where U_T is the heat of evaporation at the temperature T. Güntherschulze[12] has made use of such a cycle to compute ϕ_{+0} for those elements where the remaining data were available. With the ϕ_{+0} determined as above for molybdenum, all the terms of the cycle are known. U_T has been determined by Langmuir and Tonks,[11] V has been determined from the spectral series for molybdenum.[13] At zero degrees, $\phi_{-0}=4.42$ volts, $V=7.35$ volts, $U_0=6.33$ volts. We note then that

$$V+U_0=7.35+6.33=13.68$$

$$\phi_{+0}+\phi_{-0}=6.09+4.42=10.51$$

and that the cycle (9) *fails to close* by some 3.17 volts. Although the ionization potential for tungsten has not been determined it can be estimated as about 7.1 volts, and $U_0=8.31$ volts while $\phi_{-0}=4.53$. For tungsten we have

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[12] Güntherschulze, Zeits. f. Physik **31**, 507 (1925).

[13] Compton and Mohler, Nat. Res. Council Bulletin No. **48**, 81.

$$V+U_0=7.1+8.31=15.41$$

$$\phi_{+0}+\phi_{-0}=6.55+4.53=11.08.$$

Again the cycle does not close by some 4.33 volts.

Since the value of ϕ_{+0} which has been determined depends so greatly on the theoretical equation used, and the effect of a possible surface heat of charging and its variation with temperature, a check was made by computing the values occurring in Eq. (9) at a given temperature. In order to do this the Clausius-Clapeyron equation,

$$L_T=T(V-v_0)(dp/dT) \tag{10}$$

was used, where L_T is the heat of evaporation at the temperature T, V the volume of the vapor, v_0 the volume of the metal and p is the vapor pressure. Neglecting v_0 and setting $V=kT/p$ we have

$$L_T=\frac{kT^2}{p}\frac{dp}{dT}=kT^2\frac{d(\log_\epsilon p)}{dT}\cdot \tag{11}$$

We may express p in terms of the positive ion current by the relation (5), obtaining:

$$\log p=\log\left\{\frac{\beta}{1-r}IT^{1/2}\right\} \tag{12}$$

where β is a constant. If r does not depend on T then Eq. (11) becomes:

$$L_T=kT^2\frac{d}{dT}(\log_\epsilon IT^{1/2}).$$

This gives L_T in terms of the positive ion current measured and the temperature, and does not depend on any assumptions made concerning the surface heat of charging. Changing to logarithms to the base 10 and expressing L_T in terms of volts we have:

$$\phi_{+T}=1.987\times10^{-4}T^2\frac{d}{dT}(\log_{10}IT^{1/2}). \tag{13}$$

The values of $\log_{10}IT^{1/2}$ were plotted against T for molybdenum and the slope of this curve was determined at 2350°K. Using this slope, ϕ_+ at 2350° was found to be 5.43 volts.

The electron work function ϕ_- at 2350° was computed from Eq. (3) assuming that the specific heat of the electrons in the condensed state was zero. It's value was found to be 4.92 volts. The value of U at 2350° was also computed by means of Eq. (3) in which the integral, $\int_0^T C_{pm}\,dT$ for Mo was obtained from the work of Jones, Langmuir, and Mackay.[10] At $T=2350°$, U was found to be 5.41 volts. It is readily seen that if these values are substituted in the cycle (9) it still *fails to close* by some 2.45 volts. The failure of the cycle to close is, therefore, not due principally to our lack of knowledge concerning the surface heat of charging.

Under the assumption that C_{pp} equals zero Eq. (3) assumes the form

$$L_T = L_0 + \frac{5}{2}kT - \int_0^T C_{pm} dT. \tag{14}$$

The value of $\int_0^T C_{pm} dT$ for Mo was determined as stated above. Converting L_T to volts, Eq. (14) becomes,

$$\phi_{+T} = \phi_{+0} - 2.71 \times 10^{-4} T - 5.37 \times 10^{-8} T^2 + 0.019. \tag{15}$$

If C_{pp} is really zero then Eq. (15) should yield the same value of ϕ_+ at 2350° as Eq. (13). Using the value of ϕ_{+0} already determined (6.09), ϕ_{+T} from Eq. (15) at 2350° is 5.17 volts as compared with 5.43 volts determined from Eq. (13). The difference between these two values represents a contribution due to surface charging, thus indicating that heat is absorbed in the process. By combining Eqs. (13) and (3) it would be possible to determine an empirical value for the $\int_0^T C_{pp}\, dT$ which in turn would modify the equation used to determine ϕ_{+0} and therefore yield a slightly different value for ϕ_{+0}. It does not seem desirable to do this until the theoretical form of C_{pp} is determined because the empirical relation could be expressed in several different forms which have no obvious theoretical significance.

It should be noted that ϕ_{+T} as expressed in Eq. (13) is independent of the reflection coefficient as a result of the *assumption* that r was independent of T. It is not at all unreasonable to suppose that r varies somewhat with the temperature but it would have to vary with *extreme* rapidity to yield a value of ϕ_{+0} which would satisfy the energy cycle (9). Such an extreme variation in r is not found in the evaporation of neutral atoms or electrons and therefore may be regarded as untenable in the case of ionic evaporation. It is therefore apparent that in Eqs. (7) and (8) there are no terms missing which change violently with the temperature and thus yield a value of ϕ_{+0} sufficiently large to close the energy cycle (9).

Possible Effects of the Filament Surface

It is well known that the condition of the filament surface affects the electron emission very greatly. The ordinary thermionic work function of a filament can be varied within wide limits by allowing a monatomic layer of foreign atoms to deposit on its surface. Such a layer of thorium on tungsten reduces the work function from 4.53 volts to 2.69 volts. On the other hand a layer of oxygen on tungsten increases it to 9.2 volts. Since the positive ion work function is related to the electron work function by Eq. (9) it follows that impurities on the surface would effect the positive ion work function materially. It could be supposed for example that the positive ions were really coming from small patches of the filament which were coated with oxygen atoms. For a tungsten filament coated with oxygen $\phi_{-0} = 9.22$ volts. Using this value of ϕ_- in Eq. (9), ϕ_{+0} comes out to be 6.2 volts which agrees fairly well with the value 6.55 volts determined by experiment.

If surface contamination is the cause of the discrepancy between the work function determined experimentally and that calculated from the cycle, it is difficult to see how it could be due to oxygen. In the first place, as far as the writer is aware, it is impossible to keep oxygen atoms on the surface of tungsten at temperatures above 2300° or 2400°. In order to be sure that oxygen was not playing any part in the positive ion emission, a small amount of oxygen was admitted while the tungsten was emitting positive ions but the ion current was not affected until sufficient oxygen was admitted sensibly to cool the filament. A small amount of argon was admitted in the same way but the only effect was to decrease the ion current if an excessive amount was admitted. Argon is chemically inactive and its only action was probably a cooling of the filament.

It might be supposed that the surface of the filament was rough and jagged when looked at through a microscope and that the ions were being emitted from these microscopic points in the same way as electrons are emitted from cold metals. In the latter phenomenon, however, the electrons are emitted from the points because the field strength is extremely high at the point. In the case of positive ions however the voltage applied between the collector and filament was never greater than 150 volts and Mitra has shown that the ion current saturates very well thus making the correction for the Schottky effect very small. Furthermore tungsten undergoes a recrystallization at about 2800°K and filaments that have been made rough by ion bombardment can be made smooth again by raising the temperature above 2800°K. No extraordinary behavior of the ion current was noted in the neighborhood of this temperature.

RECOMBINATION AT THE FILAMENT SURFACE

If an appreciable amount of recombination took place at the surface of the filament, then it would be possible that the positive ion current as measured would not correspond to the actual rate of emission. The rate of recombination would be a function of the temperature and would modify the ion current in such a way that the measured ion current would not yield the true work function. The order of magnitude of this rate can be calculated from the Thomson theory of recombination. Such a calculation shows that at 2500°K the fraction of the ion current actually emitted which would be removed by recombination is $6.5 \times 10.^{-7}$ It is therefore seen that recombination does not measurably influence the measurement of the positive ion current.

PROBABLE IONIZATION OF ATOMS AFTER EVAPORATION

One may reasonably ask whether the ions might not be formed from atoms after they evaporated. Ions certainly exist in the vapor of metal in equilibrium with the metal itself, if the temperature is high enough even though the metal emits electrons but no ions. The concentration of positive ions in such a vapor may be obtained from Saha's ionization equation, and some idea of the rate of formation of ions in such a vapor may be obtained by calculating the number of collisions which occur with sufficient energy to ionize, and the number formed by the action of radiation from the hot metal. Such calculations have been made by the writer with the result that the maximum rate of formation of ions from neutral atoms in the vapor is entirely negligible compared to the ion currents measured.

PHOTOELECTRONS FROM THE COLLECTING ELECTRODE

The effect of radiation from the filament in producing photoelectrons from the collecting electrodes which would thereby influence the ion current measured has been investigated in several ways. In the first place Jenkins applied a magnetic field at right angles to the ion current in his Coolidge x-ray tube which was of sufficient strength to prevent electrons leaving the cathode from arriving at the target when a positive potential was applied to it equal to the negative potential used to collect the ions. This had no effect on the ion curent which could be true only if heavy ions alone were conducting the current. Similar magnetic experiments performed by the writer produced no effect on the ion current. Collecting electrodes of different metals were used but they produced no changes in the ion current or the variation of it with temperature. The photoelectric effect does not therefore account for a measurable part of the current observed.

POSSIBILITY OF AN APPARENT WORK FUNCTION

It appears then that positive ions of the metal are actually emitted from the metal and the amount of heat required to emit them is less than the amount deduced from cycle (9) the latter of which should be the true heat required. It seems necessary in order to overcome this discrepancy to assume that the value of ϕ_+ obtained from cycle (9) is the true work function for positive ions while the value ϕ_+ determined from the positive ion current is an apparent work function, just as it was necessary to assume in the Sommerfeld[14] theory of the Richardson effect that the true electron work function is W_a, and the value ϕ_{-0} determined by actual measurement is only apparent. In the Sommerfeld theory

$$\phi_{-0}=W_a-W_i$$

Where W_a is the true work required to remove an electron from the metal and W_i is the maximum energy which the electrons already have in the metal due to their high velocities acquired as a result of the velocity distribution law of the Fermi Statistics. It should be pointed out that W_a should not replace ϕ_- in cycle (9) because ϕ_- actually represents the work required to remove an electron which already has the energy W_i. The term W_i occurs implicitly in cycle (9) in the heat of condensation term U, since in condensing the atoms together to form the metal, part of the heat U must have been used up in giving the free electrons the energy W_i.

In the case of positive ions, the degeneracy condition which gave the electrons their high internal energy W_i, is not fulfilled due to their large mass, and their internal energy is the relatively small amount given by classical theory. Hence the question concerning a W_i for ions does not arise. However if it is to be assumed that ϕ_{+0} is an apparent work function then there must

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[14] Sommerfeld, Zeits. f. Physik **47,** 27 (1928).

exist a source of energy of an amount ψ, which is not included in one of the terms in Eq. (9) and the magnitude of which is equal to that required to close the cycle (9). Such an amount of energy could not be supplied through the agency of a force field tending to repel the ion from the metal since such energy would be implicitly included in the work function ϕ_+.

It may be that tungsten and molybdenum slowly recrystallize in an irreversible manner at high temperatures yielding the necessary energy ψ to emit an ion. The ions would thus be emitted as a secondary effect. In all probability some electrons and atoms would be emitted as a result of the recrystallization but the number thus emitted would be small compared with the number actually emitted per second per cm^2 and would not therefore measurably effect the heat of evaporation of atoms or the electron work function. This may readily be seen by noting that at 2500°K, 3.52×10^{16} atoms of Mo evaporate per sec per cm^2 while only 1.53×10^{11} ions are emitted.

It must be concluded from the foregoing investigation that some, if not all, hot metals emit positive ions of their own metal as well as neutral atoms and electrons. The analysis made above shows that the mechanism of emission of electricity from hot metals is not clearly understood especially as regards the emission of positive ions, for, unlike the evaporation of electrons and neutral atoms, the evaporation of ions is not strictly represented by an equation based upon thermodynamical arguments under equilibrium conditions.

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