in the case of $N=150$ and uniform sources, the second column of Table III gives the results of an approximate calculation for the transmission ratios. The calculation has been made by averaging an upper and lower linear approximation to the curve shown in Fig. 1 (z-scale) for $N=150$. It is evident from Table III that $f=1+(\frac{3}{2})\alpha$ is again a better approximation to the $N=150$ case than the Fermi relation, and that the $N=\infty$ case follows closely the Fermi-Amaldi transmission ratios. Further possible applications of the exact solutions, such as in nuclear level widths,[34] will not be considered at this time.

OCTOBER 1, 1940 PHYSICAL REVIEW VOLUME 58

Temperature Dependence of the Work Function of Tungsten from Measurement of Contact Potentials by the Kelvin Method*

JAMES G. POTTER**

Sloane Physics Laboratory, Yale University, New Haven, Connecticut and Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

(Received March 13, 1940)

The Kelvin method for the determination of contact potentials is adapted for measurements between filaments in vacuum. Measurements between a heated and a cool tungsten filament indicate an increase in the work function of tungsten, with temperature, of 6.3×10^{-5} volt per degree centigrade. This effect is distinguished from changes in work function arising from variations, with temperature, in contaminating layers on the tungsten, which tend to obscure the true temperature coefficient even under the best vacuum conditions. The observed true temperature coefficient appears to be comparatively independent of the existing degree of surface contamination. This suggests that the temperature effect must reside primarily in the thermodynamic potential of the electrons inside the metal and not in the potential barrier at the surface. The coefficient obtained resolves the discrepancy between the experimental value of A in the Richardson equation and the theoretical factor of 120 without the introduction of a reflection coefficient.

An increase in the electronic work function of tungsten, with temperature, of approximately 6×10^{-5} volt per degree centigrade was estimated by Waterman and Potter[1] in 1936 from data they obtained from measurements of contact potentials employing the Kelvin method. This positive temperature coefficient of the work function was in definite disagreement with a negative coefficient of approximately 4×10^{-4} volt per degree reported for pure tungsten, earlier in the same year by D. B. Langmuir.[2] His calculations were made from shifts of thermionic curves attributed to changes in contact potential between a collector and an emitter. Although Langmuir expressed the opinion that the negative coefficient might be an effect resulting from imperfect vacuum conditions, this coefficient did agree well with some deductions of Nottingham.[3]

As pointed out by Becker and Brattain,[4] if the work function, w, is of the form, $w=w_0+\alpha T$, α being the temperature coefficient and T the absolute temperature in °K, then when w appears in the exponent of the Richardson equation, the effect of the second term in w is to multiply the theoretical thermionic current by the factor, $e^{-\alpha/k}$, where k is Boltzmann's constant. After the value of 6×10^{-5} volt per degree had been reported for α in the case of tungsten,[1] it was noticed that this value made the factor, $e^{-\alpha/k}$,

---

* Part of a dissertation presented to the Faculty of the Graduate School at Yale University in candidacy for the degree of Doctor of Philosophy.

** Now at South Dakota State School of Mines, Rapid City, South Dakota.

[1] A. T. Waterman and J. G. Potter, Phys. Rev. **51**, A63 (1937).

[2] D. B. Langmuir, Phys. Rev. **49**, 428 (1936).

[3] W. B. Nottingham, Phys. Rev. **49**, 78 (1936).

[4] J. A. Becker and W. H. Brattain, Phys. Rev. **45**, 694 (1934).

practically equal to $\frac{1}{2}$. If, as is likely, the reflection coefficient at the surface of pure tungsten is almost negligible for thermionic electrons, this factor accounts for the discrepancy between Dushman's constant factor, 120, in the Richardson equation and the accepted experimental factor of $A=60$ for tungsten. In view of the ability of the positive coefficient to explain this discrepancy notwithstanding its disagreement with the coefficient of Langmuir and Nottingham, improved techniques have been employed in a new independent determination.

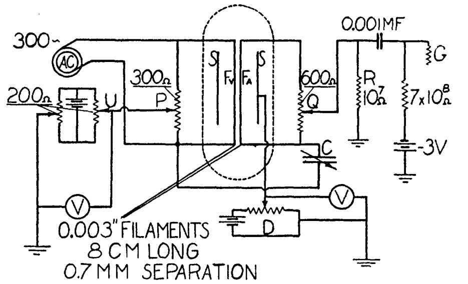

FIG. 1. Circuit for the measurement of contact potentials between filaments in vacuum by the Kelvin method. The amplifier is not shown beyond the grid of the first tube.

METHOD

The Kelvin method has again been used because it affords practically instantaneous determinations of contact potentials, allowing distinction between rapid and gradual changes of work function. In the Kelvin method the two bodies differing in work function form a condenser, which tends to become charged to their contact difference of potential, equal in magnitude to the difference in the work functions of the two bodies. When the contact potential is compensated by an applied potential, a change in capacity between the two bodies is accompanied by no electrical change.

In 1932 Zisman[5] devised a system for measuring the contact potential between two parallel plates, whereby he varied their capacity at an audiofrequency, by causing one plate to vibrate on the end of a flexible reed. The other plate was coupled to an audiofrequency vacuum-tube amplifier. An applied potential in series with a high resistance between the plates was adjusted until no signal appeared in the amplifier. At this point the applied potential had the value of the contact potential difference between the plates.

In the present investigation this method is modified to admit the measurement of contact potentials in vacuum under conditions in which the metals can be treated to yield the accepted values of the thermionic constants. Three-mil tungsten filaments approximately 8 cm in length replace the parallel plates of the above method. During measurements, one of the filaments is simultaneously heated to any desired temperature and vibrated by passing an alternating current through it in the presence of an applied magnetic field.

The electrical arrangement is indicated in Fig. 1. The two filaments, suspended parallel in one horizontal plane with a separation of 0.7 mm, appear at F_V and F_A. Above and below the filaments, outside the vacuum tube, are supported electromagnets, not shown in the figure, which maintain a steady magnetic field perpendicular to the plane of the filaments. By adjusting the strength of this field and the frequency of the current delivered to the filament, F_V, by the generator, *AC*, F_V may be set into resonant vibration in its fundamental mode, in a horizontal plane at any temperature above 300°K, with an amplitude such that it barely avoids striking F_A at its mid point. F_A is connected to ground at the midpoint, *Q*, of a shunt through a high resistance, *R*, and is coupled through a condenser to a two-stage inductance-coupled audiofrequency amplifier with earphones at the output. For clarity, the amplifier beyond the grid, *G*, of the first tube is omitted from the figure.

In order that the alternating voltage applied to F_V will produce no disturbance in the amplifier, the midpoint of this filament must be maintained at a steady potential. The midpoint may be described as that point on the two sides of which $\int Idrdc$ is the same, where Idr represents the potential drop at any instant along an element of the vibrating filament, and dc is the capacity between that element and the other filament.

When measuring the contact potential between the two filaments, the midpoint of the vibrating filament is picked up by trial at the point, *P*, on the slide wire in parallel with the filament, and its potential relative to ground is adjusted on the

---

[5] W. A. Zisman, Rev. Sci. Inst. 3, 367 (1932).

potential divider arrangement at U until there is no signal in the amplifier. With this adjustment, the net electric flux between the two filaments is zero throughout the cycle of vibration. The applied potential, which is read directly on the voltmeter, V, connected between P and ground, is then equal to the contact potential between the vibrated filament at any chosen temperature and the filament at room temperature, connected to the amplifier. If the applied potential which will eliminate the signal when the filament is at a different chosen temperature is then found, the difference in the two potentials is equal to the change in work function of the vibrating filament resulting from its change in temperature.

Obviously, the electrical midpoint of the filament should coincide with the geometrical center of symmetry throughout each vibration. Compensation for any accidental slight departure from symmetry in the construction of the tube is effected with the small auxiliary capacity, designated by C in Fig. 1, between the leads to the filaments at one end outside the tube. In the event of an incorrect setting for the auxiliary capacity, C, or for the point of contact, P, of the vibrating filament, a disturbance from the alternating potential applied to the filament enters into interference effects with the disturbance arising as a result of the change of capacity between the filaments during vibration when the contact potential between the two filaments is not exactly compensated. A reversal of the applied magnetic field, however, reverses the phase of the vibration, and hence, of the latter disturbance, without affecting the former. As would be expected, when the vibrated filament is picked up at a point remote from its true electrical midpoint, a different value of potential has to be applied to the filament to suppress the signal in the amplifier with each of the two orientations of the magnetic field. As the true midpoint is approached, the two values of apparent contact potential converge on the true value. Accordingly, reversing the magnetic field serves as the critical test while adjusting for symmetry.

Although the tube and circuits are fully shielded in copper while measurements are being made, the shield inside the tube, designated by S in Fig. 1, is desirable. If there is an appreciable field arising from contact potential, or applied potential, between the filaments and their environment, any movement of the vibrating filament will, in general, result in an immediate change in the potential of the filament connected to the amplifier, since the latter is insulated except for the high resistance to ground. This effect may require that a potential very different from the true contact potential between the filaments be applied to the vibrating filament in order to prevent a signal in the amplifier. In any accurate measurements of absolute values of contact potentials by the Kelvin method it is essential that external fields be eliminated by surrounding the specimens with an electrostatic shield to which is applied a potential equal to the contact difference of potential between the shield and the specimen connected to the potential detector, in the present case, the filament, F_A. This fact has been ignored by many users of the Kelvin method, and instances may be cited in which shields involved in comparatively large changes of capacity with the moving element have been grounded instead of being held at the correct potentials. According to measurements made in the present investigation, this leads to absolute values for contact potentials in considerable error. The shield may be set at the correct potential for measurements at all temperatures of the vibrating filament by adjusting it until the contact potential between the filaments measures zero when both filaments are practically cold and contaminated to the same degree. The potential of the shield may also be set from a knowledge of its work function and that of the filament connected to the amplifier, but contamination effects limit the accuracy of this latter method. When, as in the present project, attention is restricted to changes in work function involving only differences in contact potentials, the value of the potential of the shield is not important since it affects the absolute magnitude of all the contact potential measurements by the same additive amount.

Equipment and Experimentation

In the design of the vacuum tube for the filaments and shield, primary consideration must be given to the maintenance of symmetry. For high sensitivity, the capacity between the elements of the circuits connected to the two filaments is kept as low as possible in order that the change of capacity during vibration may be a large fraction of the total capacity. The tension on the filament which is vibrated has to be maintained with considerable precision, the most practicable value turning out to be about seventeen grams. This gives the filament a natural fundamental frequency of vibration of approximately 300 cycles per second. Such a tension, however, is impossible when the filament is heated to a high temperature for the purpose of outgassing.

The foregoing considerations lead to radical departures from conventional vacuum-tube design. The horizontal filaments and concentric cylindrical shield are supported by a glass rod framework, suspended from the ends of the tube. The portions of the filaments between which the capacity is altered by vibration are confined between small horizontal quartz rollers. In passing over the rollers, the filaments rest in peripheral grooves ground to maintain their proper spacing. The rollers allow the filaments to expand with temperature without changing the length of the segments between which the capacity is varied. A short distance beyond the rollers, the ends of the filaments are led off in opposite directions to the sides of the tube through capillaries. One capillary for each filament, but at opposite ends, is fastened rigidly to the frame. The second capillary for each filament, which is allowed to swing freely below the rollers, has fastened to it a weight that maintains the tension in the filament. The capillaries, which fit the filaments snugly, anchor them to the frame and weights with the introduction of a minimum amount of capacity which does not vary during the vibration. Beyond the capillaries the ends of the filaments are connected to tungsten leads sealed into the sides of the tube. The fact, that the vibrated segment of the filament is held fixed at its ends by the quartz rollers, minimizes error in measurement from end effects.

While a filament is heated to a high temperature during outgassing, a partial support is introduced under the weight used to maintain the tension in the filament during vibration. The support is attached to a lever carrying a counterweight on the opposite side of a bearing, the bearing being somewhat above the center of gravity of the weight and counterweight so that, as the filament elongates, the lifting moment of the counterweight increases. The support is withdrawn when the filament is to be vibrated, the counterweight being propped up by a cam. Both the cam and the support are moved into position by levers carrying iron armatures which are pulled by magnets manipulated outside of the tube. To minimize the problem of outgassing, the armatures and counterweights are encased in glass. The levers, also of glass, are operated on sleeve bearings of glass.

With a view to detecting possible effects from imperfect shielding, two different designs of shield have been tried inside the tube. The shield is a hollow cylinder, approximately 4 cm in diameter, surrounding the portion of the filaments between the quartz rollers. The cylinder is partially closed at its ends, holes being left for the passage of the filaments. In one design, the shield was of glass, which was given a coating of evaporated silver after a satisfactory vacuum had been obtained. Small shadow casters prevented the deposition of silver from the molten source onto the quartz rollers. In the other design, the shield was fashioned from a sheet of tantalum. This shield was outgassed at a yellow heat by electron bombardment from the filaments employed in the contact potential measurements. No difference was discerned in the results obtained with these two types of shield.

Three-mil tungsten wire from a number of sources has been tried for the filaments. All of the specimens of wire have been found to develop inhomogeneities and regions of brittleness after any program of heating in vacuum, for the purpose of outgassing. When brittleness occurs at locations subjected to considerable mechanical disturbance, the filaments fail before data can be taken. Three sets of filaments have permitted the taking of data, while after fourteen other successful attempts to assemble and evacuate the tube, filament failures prevented the taking of data. The most satisfactory wire has been that prepared especially for the work through the courtesy of Dr. W. L. Enfield and Mr. W. P. Zabel of the Nela Park Laboratory of the General Electric Company. According to Mr. Zabel, this wire is prepared by oxidizing the black drawn "218 wire" in air, for roughly $\frac{3}{4}$ of a second at a temperature of 800°C and then annealing and cleaning it in wet hydrogen for $1\frac{1}{2}$ seconds at 2000°C.

Filament temperatures throughout the investigation were determined from filament currents with the aid of the tables prepared by Langmuir and Taylor[6] and Langmuir and Jones.[7]

In the course of the investigation two kinds of pumps have been employed: a two-stage mercury diffusion pump and a three-stage diffusion pump operating with organic fluids, essentially of the design devised by Hickman.[8] Following a preliminary dehydration of the entire vacuum system by the application of heat while the forepump is in operation, a bake for about 48 hours at a temperature between 475° and 500°C is given the main tube as well as an ionization gauge and an adjacent trap. Refrigerant is maintained on a second trap, next to the diffusion pump, which is in operation during the baking. Near the middle, and again, at the end of the period of baking, all metal parts are heated by conduction or electron bombardment. The filaments are heated for a total period of about 10 hours at a temperature of 2400°K, for a period of two hours at 2600°K, and for a brief interval at 2900°K, refrigerant being applied to the trap closer to the tube before the heating schedule is completed. This procedure results in a pressure ranging between 1.4×10^{-8} and 7×10^{-9} mm of mercury, which obtains as long as the pumps are in operation throughout the duration of the experiment. The lower figure for the pressure has been realized only with the organic fluid diffusion pump, but it has been achieved under optimum conditions with each of three commercial types of organic pumping fluid when the traps are refrigerated with dry ice. It is believed that this lower figure does not understate the pressure since it is determined with an ionization gauge which has been calibrated by several groups of investigators from pressures existing when a mercury diffusion pump is used. The high probability of ionization of the organic molecules of the pumping fluid compared to that of mercury would tend to make the pressures read high in the present instance.

The employment of liquid nitrogen, instead of dry ice as a refrigerant with the organic pumping fluid, results in no measurable change in the magnitude of the pressure indicated by the ionization gauge, but it does eliminate some small component of the residual vapor which profoundly alters the contamination effects of the vapor on the filaments. Measurements of contact potential, when using the colder refrigerant, can be interpreted on the basis that the contaminating layer which forms on the filaments, after they have been flashed at a high temperature and then allowed to cool, results in a gradual increase in the work function of the filaments. A steady state is attained after about a day, when the work function appears to have been increased by several tenths of a volt. When a mixture of dry ice and acetone replaces the liquid nitrogen on the trap, the behavior of the contact potential suggests that the work function increases to a maximum value in a few hours following a flashing of the filaments and then gradually decreases for a number of days before the contamination has reached an equilibrium condition. Thus, experimentally, the removal of contaminating agents by moderate heating of a filament may either increase or decrease its contact potential depending upon the stage of its contamination.

More significant than the change with contamination, there is a second superimposed change in contact potential whose direction and magnitude is always uniquely determined by the change in temperature of the filament. Whereas the change attributed to contamination transpires comparatively slowly, especially following a reduction in temperature of the filament, this second change in contact potential immediately accompanies a variation in the temperature of the filament. This change is interpreted as a modification with temperature, in the metal itself, and thus gives a measure of the temperature coefficient of the work function of tungsten, α.

Although the variation in work function attending the driving off or return of contamination when the temperature is altered is, in general, larger than the change in work function determining α, the latter can often be clearly differentiated from the former by making a rapid

---

[6] I. Langmuir and J. B. Taylor, Phys. Rev. **50**, 68 (1936).

[7] I. Langmuir and L. A. Jones, Gen. Elec. Bull. 419 (Sept. 1927).

[8] K. Hickman, Synthetic Organic Chemicals **9**, 1 (1935).

TABLE I. *Changes in contact potential from contamination effects and effects characteristic of tungsten, following changes in temperature. T, temperature in °K; S, seconds since last alteration of temperature; V, contact potential of heated filament in volts. Changes determining temperature coefficient of tungsten are in italics.*

A											
T	300	935	935	300	300	300	300	300	300	935	300
S		30	180	35	50	65	90	100	300	30	40
V	0	−0.26	*−0.26*	*−0.30*	−0.30	−0.26	−0.18	−0.16	−0.16	*−0.26*	*−0.30*
B											
T	300	935	935	935	935	300	300	300	300	300	
S		30	55	80	300	25	55	135	150	600	
V	*−0.26*	*−0.22*	−0.24	−0.26	*−0.26*	*−0.30*	−0.30	−0.26	−0.26	−0.26	
C											
T	935	935	300	300	300	300	300	300	300		
S		120	30	120	225	300	380	435			
V	0.76	*0.76*	*0.72*	0.72	0.70	0.66	0.62	0.56	0.56		
D											
T	935	300	300	300	300						
S		20	60	180	360						
V	*0.46*	*0.42*	0.42	0.42	0.36						
E											
T	935	300	300	300	300						
S		17	40	60	135						
V	*−0.32*	*−0.36*	−0.32	−0.26	−0.26						

series of determinations of contact potentials with an accurate record of the time of each determination. Some representative sets of determinations, from which the distinction between the two types of change may be appreciated, are presented in Table I. They are all selected to cover the same temperature interval, but different stages of filament contamination. Each row designated by *T* lists the successive temperatures, in °K, of the vibrating filament. *V* is the potential in volts applied to this filament to obtain a minimum signal in the amplifier, that is, the contact potential between the vibrating filament and the stationary filament which is at room temperature. The instant at which the contact potential is measured is indicated by *S*, the number representing the time interval in seconds which has elapsed since the temperature of the filament was last altered. For example, the set of data under *A* was taken when the contamination was at a stage to indicate a decrease of work function with increase of temperature. The first entry, made after both filaments had been left unheated to accumulate equal amounts of contamination for several hours following their flashing at 2900°K, indicated that the apparatus was in adjustment to register zero contact potential when the vibrated filament was at 300°K, practically the temperature of the other filament. As shown in the table, when the temperature of the vibrated filament was subsequently raised to 935°K, a measurement completed 30 seconds later revealed a contact potential of −0.26 volt, which persisted until the filament was cooled 180 seconds after it had been heated.

Comparison with subsequent data will show that the reduction in work function signified by the foregoing change in contact potential should be attributed primarily to the driving off of contamination from the filament by the application of heat. A measurement of −0.30 volt, made 35 seconds after the filament had cooled, disclosed that the cooling had reduced the work function 0.04 volt. Although a reading 15 seconds later detected no change in the contact potential, an observation 65 seconds after the filament had cooled showed that a new trend toward a higher quasi-stable value of work function was in progress. The above 0.04-volt transition in work function, which is in italics in the table and is repeated identically in a second temperature cycle recorded in italics at the end of the first set of data, was reproducible indefinitely on the occasion from which the above sample of data was taken. The fact that this transition always seemed to accompany, and go to completion with, the cooling of the filament whereas the subsequent reversal in the trend of the work function always began gradually after the filament had cooled, indicated that the former was a genuine temperature effect in the metal itself while the latter was the effect of a redeposition of contaminating layers on the surface.

Although, as would be expected, the changes in work function attributed to the driving off of contamination from the filament, when its temperature was raised, were, in general, more rapid than the changes attributed to the return of contaminants to the cool filament, there were occasions when the first mentioned changes were slow enough to be followed. The set of data under *B* in Table I is an example. This sample of data is taken from an occasion when the contaminations of the filaments resulted in a comparatively stable contact potential of -0.26 volt with both filaments at room temperature. Here the stage of contamination was such that its alterations with temperature gave rise, comparatively slowly, to variations in work function which exactly nullified the immediate changes with temperature in the work function of the metal itself. The transitions recorded in italics, which are instances of the true temperature effect, are obviously of a different nature from the slow changes in the opposite direction which follow them.

The set of data under *C* reports a stage where the modifications of work function from contamination effects are in the same direction as the modifications from the behavior of the metal itself but are still less rapid than in the preceding examples. On this occasion the contaminations gave rise to a comparatively stable contact potential of 0.56 volt when both filaments were at room temperature. A similar situation is reported under *D* with somewhat lower absolute values of contact potentials.

The foregoing examples are typical of data taken from the equipment over practically the same temperature interval in more than one hundred different instances. It is significant that, regardless of the stage of contamination, the same 0.04-volt change in contact potential consistently appears immediately with the 635-degree change in temperature whenever it is not masked by the always irregular contamination effects. Moreover, this contact potential change seems to be independent of the absolute magnitudes of the contact potentials, which are governed by the contamination history of each filament and vary widely in the course of time.

Although it would be desirable to have data on a filament absolutely free of contamination, the foregoing fact reduces the importance of such data. After the contamination effects were understood, attempts were made to obtain data on the true temperature effect on the work function of a filament immediately after it was heated to a high temperature, but the rapidity of the contamination changes, which always occurred immediately following such a heating, defeated all attempts until filament failure terminated the investigation. Data obtained with a minimum of delay, after the filaments were outgassed, are recorded under *E* in Table I. On this occasion observations were commenced twenty minutes after the filaments had been cooled from a temperature of 2900°K. Although the initial measurement, made with both filaments cold, showed zero contact potential, the contact potentials shifted rapidly and erratically on heating, and it was not until twenty minutes later that they showed any stability at moderate temperatures and the recorded data were obtained.

Most of the data have been taken with the shield inside the tube grounded. Since the work function of tantalum differs from that of tungsten by only a few hundredths of a volt, grounding should give the proper potential to the tantalum shield, to within the accuracy sought. When the two filaments and shield had been recently outgassed and the subsequent treatment of the two filaments was identical, the contact potential was always found, appropriately, to read zero with the tantalum shield directly grounded. With contamination on both the shield and the filament connected to the amplifier, the potential to be applied to the shield to give correct absolute values of the contact potentials between the filaments becomes problematical. However, since differences in contact potentials, and not absolute values, are of interest in the present investigation, the potential setting of the shield becomes unimportant. As would be expected, data show that the effect of changing the potential on the shield is simply to shift the apparent absolute magnitude of the contact potentials, the apparent

TABLE II. *Temperature coefficient of work function of tungsten for various observed temperature intervals.*

T_1	935	588	675	695	937	932	935	1025	1120	1260
T_2	300	387	303	308	387	587	802	308	398	308
V_1	0.36	0.474	0.280	0.344	1.040	0.60	0.496	1.16	1.064	−0.32
V_2	0.32	0.460	0.256	0.320	1.006	0.58	0.486	1.10	1.004	−0.40
$\alpha\times10^5$	6.3	7.0	6.4	6.2	6.2	5.8	7.5	8.5	8.3	8.4

shift in contact potential being approximately one-tenth the change in potential on the shield and in the same direction. The immediate change in contact potential accompanying a variation in temperature is found to be independent of the potential on the shield. Thus, the data show one occasion when a potential of -3 volts applied to the shield reduced the apparent contact potential of the vibrated filament to zero with the filament at a temperature of 300°K. With an increase in its temperature to 935°, the contact potential of the filament became 0.04 volt.

Although the most intensive study of contact potentials with the equipment was conducted over the temperature interval just quoted, scattered measurements were made over other temperature intervals. Some representative data on these temperature intervals are included in Table II, where, in each column, V_1 and V_2 are the contact potentials, in volts, observed immediately before and after the temperature of the filament is changed from T_1 to T_2 and α is the change of work function, in volts per degree centigrade, computed from the data in the column. The first column gives, for comparison, typical data on the interval discussed heretofore in more detail.

It will be noted that the data involving temperatures above 935°K do not give values of α in agreement with those for the lower temperatures. The data, in general, indicate a higher temperature coefficient but lack reproducibility. This may be accounted for, in part, by the fact that for the higher filament temperatures the signal in the amplifier becomes less quiet when the contact potential is balanced, possibly resulting in reduced sensitivity. However, the reversal in phase of the signal arising from imperfectly balanced contact potential, when the applied compensating potential, on being increased or decreased, passes through the correct compensating value, results in a change of quality of the signal from which the correct compensating value can be quite accurately identified. The irregularity of the data at the higher temperatures may probably be attributed primarily to the formation, by thermionic emission, of an electron sheath around the heated filament. The results of Langmuir[2] for temperatures above 1000°K have been criticized on this basis.[9]

Even though the results for the higher temperatures are not considered, an evaluation of the accuracy of the data below 935°K is not simple. Since, with the difficulties of the experimental work, it was not feasible to obtain systematic data over subintervals in the temperature range from 935° to 300°K, any calculation on precision from the data obtained for these subintervals would be quite artificial. Although considerable data were obtained, which are not presented in Table II, they are not extensive enough to give a fair sample of the accuracy of measurement nor to merit statistical treatment, and with single observations over a given temperature interval there is always some uncertainty as to whether contamination effects have been completely differentiated from the true temperature dependence of the work function of the metal itself. Accordingly, it seems advisable to regard these data only as a check and to base the final evaluation of the temperature coefficient entirely on the data obtained from the temperature interval, 935° to 300°K.

While the 0.04-volt change in contact potential always observed with this temperature interval appears to be only a rough approximation and the exact figure belonging in the next decimal place is admittedly not known, it becomes fairly evident from the history of the observations that this potential change cannot differ greatly from 0.04 volt. In the first place, prior to the date when it had been learned how to distinguish between the true temperature effect and contamination effects and before any attempt was made to express

---

[9] A. L. Reimann, Proc. Roy. Soc. **163**, 499 (1937).

filament heating currents in terms of temperatures, the 0.04-volt interval may be found in the data a large number of times accompanying temperature intervals which deviated, on the average, only negligibly from the above interval. After the interval was identified with the change in the work function of the metal itself, serious attempts were made to detect some slight departure from the number 0.04. Tests with the equipment showed that contact potentials could be located reproducibly to the nearest 0.005 volt; however, with this sensitivity there was obtained practically no evidence of a departure from 0.04 volt. Whereas with this sensitivity a sizable error could be consistently made in numerous observations as a result of prejudice, there is no reason to believe that the consistency of the result in the more than one hundred observations over this interval should not reduce the probability of error somewhat.

It seems reasonable, therefore, to conclude that a temperature coefficient for the work function of tungsten may be established from the results for this interval to within a probable error of ten percent. It is significant that the deviation measure of the coefficients calculable from the data taken from subdivisions of this temperature interval falls well within this ten percent limit. Accordingly, using the value in Table II, it may be stated that in the temperature range from 300° to 935°K, with a probable error of not over ten percent, the work function of tungsten increases approximately linearly with temperature at the rate of 6.3×10^{-5} volt per degree centigrade.

Discussion of Results

The examples of data in Table I indicate the magnitude of the error in determinations of the temperature coefficient of the work function which may arise from contamination effects. The observed modifications of the work function by contaminants are of the order of magnitude encountered by investigators of other electronic phenomena under the best vacuum conditions obtainable with contemporary techniques.[10, 11] They stress the desirability of a method, such as the present one, which can follow rapid changes in surface conditions. The wide divergence in the several values of the temperature coefficient of the work function of tungsten which have been noticed by other observers[2, 9, 12–14] may have its explanation in confusion resulting from a predominance of the contamination effect instead of the true temperature effect.

Attention has already been directed to the most surprising aspect of the results; namely, the apparent independence of the true temperature coefficient of the work function on the existing stage of contamination on the filament. This is in agreement with the findings of Reimann[9] published shortly after the preliminary announcement of results on the present investigation. Using thoriated tungsten over a wide range of states of activation, Reimann found a temperature coefficient of the work function which was independent of the state of activation. Reimann's method of measurement was similar to that of Langmuir.[2] The value of the positive temperature coefficient obtained, 7.5×10^{-5} volt per degree, is in fair agreement with the value, 6.3×10^{-5} volt per degree, determined in the present investigation.

The results of both investigations suggest that the temperature effect in the work function does not reside primarily in the surface potential barrier of the metal, which varies with activation and contamination, but in the energy distribution of the electrons inside the metal. If the opposite were the case, it would be difficult to understand how a change with temperature in the surface would be independent of the contamination. Interpreted in the terms of the Sommerfeld theory of metals, in which the work function is expressed in the form, $W_a - W_i$, where W_a is the amount of work which an electron at rest must do to escape from the surface and W_i is the Fermi "characteristic energy" of the electrons in the metal, the above experimental evidence implies that the temperature effect in W_i predominates over that in W_a.

The existing state of the theory of potential barriers admits of no decisive theoretical predictions on the effect of temperature on W_a.[4] On the other hand, the order of magnitude of W_i

---

[10] L. J. Haworth, Phys. Rev. **48**, 88 (1935).

[11] P. A. Anderson, Phys. Rev. **54**, 753 (1938); **57**, 122 (1940).

[12] F. Kuhn, Ann. d. Physik **5**, 15, 825 (1932).

[13] W. B. Nottingham, Phys. Rev. **46**, 339 (1934).

[14] A. King, Phys. Rev. **53**, 570 (1938).

may be computed on the simple Sommerfeld theory. Considering the effect of thermal expansion on the density of tungsten, which enters into the computation, W_i may be computed to decrease with increase of temperature by about 10^{-4} volt per degree. This would account for an increase of the same magnitude in the work function. The agreement of this figure with the experimental values for the temperature coefficient of the entire work function provides further evidence that the temperature effect in W_a is small compared to that in W_i.

It is of interest to note that the temperature coefficient for the work function of tungsten reported here is of the order of magnitude of the coefficients deduced by less direct methods for other pure metals by other investigators in several instances. Much of the data, including the preliminary result of the present investigation,[1] has been summarized and interpreted in terms of temperature coefficients in a paper by Cashman.[15] The similarity in magnitude of the coefficients for the different metals can be taken as additional support for the theory that the temperature dependence occurs primarily in W_i, since it would be expected to vary little here from one metal to another.

As shown by Cashman in the case of the coefficients for the other metals, the inclusion of a term involving the coefficient resulting from this investigation, when the work function for tungsten is introduced in Richardson's expression for thermionic emission current, completely resolves the long recognized discrepancy between the Dushman theoretical emission factor, 120, and the experimental emission factor, commonly designated by A. The effect of the temperature coefficient, 6.3×10^{-5} volt per °K, is to multiply 120 by a factor which results in the quantity, 58 amp. $\text{cm}^{-2}\,{}^\circ\text{K}^{-2}$. This is in agreement with the accepted experimental value of A for tungsten to within the accuracy of the data.

This agreement admits no appreciable reflection coefficient in the thermionic emission for pure tungsten. Although polycrystalline tungsten has been the subject of the present investigation, if the deduction may be relied upon that the temperature coefficient resides primarily in W_i and not in W_a, the results should apply to single tungsten crystals and be independent of the face considered.

An interesting aspect of the contact potential measurements, which have been presented here, is the information they provide on the magnitude of a theoretical reversible heating effect in the surface of the tungsten when charge is added to, or subtracted, from it. As deduced independently by Lorentz and Kelvin and developed recently by Bridgman,[16] the addition of unit positive charge to the surface of a metal must, whenever the operation is isothermal, be accompanied by an addition of heat equal to TdV/dT, where T is the absolute temperature and the derivative is the contact potential between two specimens of the metal differing in temperature by one degree. The derivative obtained in the present investigation indicates a "surface heat of charging"[17] for tungsten at 300°K of 1.5×10^{-12} calorie per electrostatic unit of charge. Although direct measurements of surface heat of charging seem impracticable with present techniques, Bridgman[18] suggests that values calculated from contact potential measurements may have significance in theories of the electronic structure of metals, providing for different binding forces on electrons on the surface from those existing in the interior of the metals.

The author wishes to acknowledge his great indebtedness to Professor A. T. Waterman, of Yale University, who initiated the project reported here and provided invaluable counsel throughout its execution. He is furthermore particularly indebted to Mr. F. P. Noble for his resourceful and untiring assistance in the design and construction of the glassware. Appreciation is also tendered the faculty of the University of Chicago for the privilege of using the facilities of the physical laboratory for the conclusion of the experimental work.

---

[15] R. J. Cashman, Phys. Rev. **52**, 512 (1937).

[16] P. W. Bridgman, *Thermodynamics of Electrical Phenomena in Metals* (Macmillan, 1934), p. 90.

[17] L. Tonks and I. Langmuir, Phys. Rev. **29**, 524 (1927).

[18] P. W. Bridgman, reference 16, p. 73.