

CONTACT POTENTIAL MEASUREMENTS WITH ADSORBED FILMS

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(Received March 30, 1929)

ABSTRACT

Measurements have been made of the contact potential differences between a clean unheated tungsten filament, and the same filament coated with an adsorbed film of thorium, caesium, oxygen, or a mixture of caesium and oxygen. The method used is well adapted to prevent accidental contamination of the filament surfaces. The values found for the contact potentials between cold surfaces are

Cs-O-W—W	3.1 volts
Cs-W—W	2.8
Th-W—W	1.46
W—OW	0.8

The surface on the left is positive to that on the right. These values of contact potential do not agree with those calculated from the thermionic emission constants. An example is given of the application of the method to the measurement of the changes in work function produced by heating a tungsten filament to various temperatures in presence of caesium vapor, thus changing the amount of adsorbed caesium.

THE measurement of the contact potential difference between two metallic surfaces has been a subject which has attracted the attention of experimenters for many years. Unfortunately the values obtained have been most inconsistent, chiefly on account of the great difficulty of keeping metal surfaces free from contaminating films. The great amount of experimental work with thermionic tubes during the last fifteen years has emphasized the difficulty of keeping hot filaments free from surface contamination. When the surfaces used are cold, as is usually the case in contact potential measurements, this difficulty is enhanced.

With this in mind we have made our contact potential measurements between filamentary electrodes, which can be easily cleaned by heating. Moreover, by working with adsorbed films, the surface of a single filament can be brought into different states, and the contact potential differences between these states determined. This makes the experimental tube very simple, so that good vacuum conditions are easily maintained.

The experimental method is illustrated in Fig. 1. The tube contains two cylinders c , g , and two loop filaments a , b . One of these filaments b , usually of thoriated tungsten, is maintained at a definite temperature and state of activation, and serves as a standard source of electrons. Cylinder g is fixed at a suitable negative potential with respect to b , so that no electrons can leave the part of b which is inside g . This serves to eliminate all effects occurring at the ends of the filaments, where conditions are not definite. Cylinder c , is fixed at about the same potential as the part of b which is inside c . Electrons can flow therefore from b to c or a . The surface of fila-

ment a is then put in some definite condition (for example, a complete film of thorium is formed on it¹), and a characteristic is taken of the electron flow from b to a (i_{ba}) as a function of the potential of a with respect to b (V_{ab}). The surface of a is then changed (for example, by heating to a high enough temperature to drive the thorium completely off) and another characteristic taken of i_{ba} as a function of V_{ab} . The voltage displacement of these two characteristics from one another then measures the contact potential difference between the two states of the surface of a .

An alternative procedure is to find the values of V_{ab} for the two states of a , which are required to give the same value of i_{ba} (say 10^{-6} amp.) The difference between these two values of V_{ab} gives the contact potential.

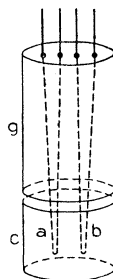


Fig. 1. Arrangement of filaments and cylinders.

It is advisable, however, to take the complete characteristics at first over a considerable voltage range, as lack of parallelism of the two characteristics is an indication of some wrong experimental condition.

Some necessary points in the experimental technique are as follows:—

(1) The vacuum must be good. The tube was immersed in liquid air during the measurements.

(2) If an alkali metal is present in the tube care must be taken to distill the metal from the surfaces of g and c , so that photoelectric currents caused by the light from the filaments will not vitiate the results. This distillation is conveniently done by warming the cylinders by radiation from one of the filaments after immersing the tube in liquid air.

(3) It is important to remove all easily volatile impurities from c and g even though the radiation from b does not cause appreciable photo-emission. If this has not been done, then when a is heated to change its surface condition, c is also heated enough to change its surface condition and a change in the electric field due to c ensues.

(4) Cylinder c must be negative to a so that secondary emission from a to c cannot occur.

(5) If very fine filaments (0.0025 cm diameter) are used the positions of the ends of the loops may change in an erratic manner when the filaments are heated to a high temperature. This change, of course, spoils the measurements.

¹ Langmuir, Phys. Rev. **22**, 357 (1923).

The measurements to be described² were made with two tubes—numbers 156 and 502.

In tube 156 cylinders *c* and *g* (Fig. 1) were of tungsten wire spirals, the idea being to insure that the caesium vapor pressure (for other experiments) inside the cylinders should be the same as that determined by the temperature of the bulb wall. Filaments *a* and *b* were of thoriated tungsten wire 0.0102 cm diameter, each containing 12.7 cm of wire. The area of the part of each filament inside *c* was 0.11 cm². The tube contained caesium. It was used on the pump and was immersed in liquid air during the measurements.

Tube 502 contained three filament loops—*a* and *d* were of thoriated tungsten wire (0.0102 cm diameter), and *b* was of pure tungsten (0.0051 cm diameter). The cylinders *c* and *g* were made of nickel sheet. This tube was

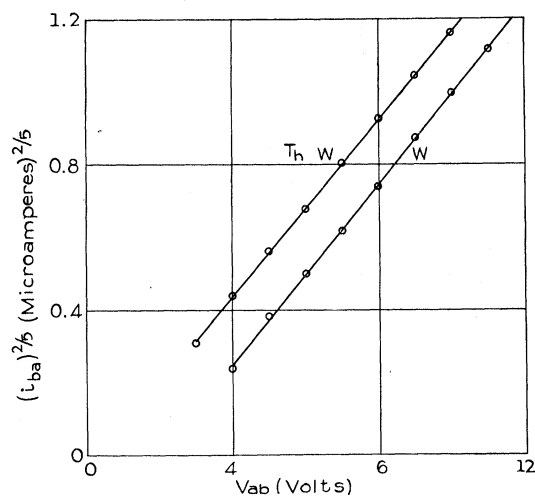


Fig. 2.

used on the pump, so that oxygen could be admitted. It was immersed in liquid air during measurements.

Measurements of the contact potential between tungsten and thoriated tungsten were made with tube 156. Filament *b* was thoriated and run at 1730°K as the standard source of electrons. The total potential drop over *b* was 5.5 volts, and that over the part of *b* inside *c* was 1.5 volts. The potential of the part of *b* inside *c* therefore ranged from +2.0 to 3.5 volts with respect to the negative end of *b*. The potential of *c* was +1.5 with respect to the negative end of *b*, so that *c* was negative to all parts of *b* inside it (apart from contact differences of potential). Therefore since the area of *c* was very large compared with that of *a*, the total field accelerating electrons away from *b* was small, even when *a* was 10 volts positive to *b* (negative end). As a result, the space charge limited current to *a* is proportional to the 5/2 power of the effective voltage accelerating electrons away from *b*. Ac-

² These measurements were made from two to four years ago. They are incomplete, and publication was delayed in the hope of doing further work. As opportunity for this has not occurred yet, it seems worthwhile to publish a description of the method and of the results obtained to date.

cordingly in Fig. 2 we plot $(i_{ba})^{2/5}$ as a function of V_{ab} in order to obtain a linear plot. Such characteristics were taken first with the surface of a completely coated with thorium, and then with the thorium removed. The other conditions were $E_o = -22.5$, $E_c = +1.5$, both with respect to the negative end of b . The two lines in Fig. 2 are parallel throughout their course and displaced from each other by 1.46 volts. This then is the contact potential difference between cold tungsten and thoriated tungsten surfaces, the ThW being positive to the W surface. The fact that the lines are parallel over the entire voltage range gives us confidence in the result. The same value for this contact potential difference was also obtained with tube 502.

Tube 502 was used chiefly to make measurements of the contact potential between tungsten surfaces, clean, or coated with oxygen, caesium, or both. Filament d was used as a thoriated electron source, while filament b was

Reference	Run	Cs OW Activated	Cs OW Unactivated	Cs W	W	OW Activated	OW	ΔV	V_c
1810	1,2		←→					3.80	1.5
1810	2,3				←→			0.70	1.5
			←→					(3.10)	
1812	6,7				←→			0.75	1.5
1814	21,22				←→			0.75	1.5
1815	1			←→				3.00	1.5
1815	2	←→						4.24	1.5
1815	2				←→			1.11	1.5
			←→					(3.13)	
1816	3	←→						3.78	1.5
1816	3				←→			0.61	1.5
			←→					(3.17)	
1817				←→				2.72	0.5
1819	1			←→				2.71	1.0
1819	2				←→			0.90	1.0
1819	3	←→						4.10	1.0
1819	3				←→			1.00	1.0
			←→					(3.10)	

Fig. 3

coated with various films. Filament a was heated to drive caesium off cylinders c and g before the measurements were started. Usually complete characteristics were not taken, but the potential of b necessary to take a certain electron current from d was found.

The measurements which were considered to have been made under satisfactory experimental conditions are listed in Fig. 3. The various kinds of surfaces are listed in separate columns, and the double arrow indicates between which pair of surfaces the measurement of contact potential difference (ΔV) was made. The values of ΔV in parentheses were obtained by subtracting the two preceding values. The cylinder potential V_c is given in the last column. V_o was kept at -22 volts throughout. The surfaces at the left of the table are positive to those at the right.

The method of preparation of the surfaces was as follows. The W surface was of course prepared by flashing filament b for a short time at a high temperature. This cleaning was always done before depositing an adsorbed

layer. The OW surface was prepared by letting oxygen come in contact with the cleaned, cold filament, the tube being immersed in liquid air to prevent rapid oxidation of the caesium in the tube. The CsW surface was similarly prepared by letting caesium vapor deposit on the cleaned, cold filament, the tube being subsequently immersed in liquid air. For the CsOW (unactivated) surface, an oxygen layer was first formed on the cleaned filament, sometimes by adsorption with the filament cold, and sometimes by heating the filament for 1 sec. at about 2000°K in a low pressure of oxygen (a few baryes). Caesium was then allowed to deposit on this surface. A surface prepared in this way is not an active thermionic electron emitter.³ To obtain large emissions it is necessary first to activate the filament by heating for a few seconds at 1600 to 1800°K. The CsOW (activated) surfaces were prepared in this way.

Suppose we started with a CsOW (unactivated) surface, as in 1810 (1, 2) of Fig. 3, and measured the potential (V_{bd}) of b necessary to draw a certain electron current (i_{ab}) from d . Filament b was then heated hot enough (up to 1600°K) to drive off all the caesium, but not to remove any large amount of oxygen. V_{bd} was then again determined for the same value of i_{ab} . The difference between the values of V_{bd} then gave the contact potential difference between CsOW (unactivated) and OW (activated), since the heating to 1600°K was considered to have put the oxygen layer in nearly the same condition as that in an activated CsOW surface. The oxygen layer was then distilled off by heating to 2500 to 2800°K for a few seconds, giving a determination of the contact potential difference between OW (activated) and W. The procedure in the other cases of Fig. 3 was analogous.

The average values of contact potential taken from all the data are:—

CsOW-W: 3.1 volts	ThW-W: 1.46 volts
CsW-W: 2.8	W-OW: 0.8

In each case the surface on the left is positive to the one on the right. Most confidence is felt in the ThW-W result. The others should be regarded as provisional values, although no reason is known for suspecting serious error.

It will be noticed from Fig. 3 that the data are not accurate enough to distinguish between the different types of OW surfaces investigated. It is more surprising that there is also no distinction between activated and unactivated CsOW surfaces, as there is a large difference (of the order 10^5 fold) between the electron emissions from these surfaces.

The contact potential differences are connected with the thermionic emission constants for the various surfaces by the relation⁴

$$\Delta V = \phi_1 - \phi_2 + (T/11600) \ln(A_2/A_1) \quad (1)$$

where ϕ_1 and ϕ_2 are the work functions of the two surfaces, expressed in volts, and A_1 and A_2 are the values of the A constant of the thermionic emission equation. The values of these constants are given in Table I, together with the temperature range over which the measurements on which the constants are based were made.

³ Kingdon, Phys. Rev. **24**, 510 (1924).

⁴ Richardson, Emission of Electricity from Hot Bodies (1921) p. 41.

TABLE I. *Thermionic constants of various surfaces.*

Surface	b degrees	ϕ volts	A amp/cm ² T ²	Temp. range °K
CsOW ⁵	8300	0.71	0.003	600–700
ThW ⁶	30500	2.63	3.0	1150–1600
W ⁷	52600	4.52	60	1900–2300
OW ⁶	107000	9.23	5×10^{11}	1500–1700

In Table II are shown the observed values of contact potential between various surfaces, together with the values calculated from Eq. (1) using the data of Table I. The contact potentials have been calculated for a temperature of 300°K in (1), since the filaments were not heated.

TABLE II. *Calculated and observed values of the contact potential for various surfaces.*

Surfaces	ΔV (calc.)	ΔV (obs.)
ThW–W	1.81	1.46
CsOW–W	3.55	3.1
W–OW	4.12	0.8

The agreement is not good. In no case was there any indication of a contact potential difference of 4 volts between tungsten and oxidized tungsten. It is believed that the differences between the observed and calculated values are well outside the experimental error in the contact potential measurements for the ThW–W and W–OW combinations. However it may not be justifiable to use electron emission constants determined at elevated temperatures to calculate contact potential differences between surfaces at room temperature. An attempt was made to measure contact potentials between hot surfaces, but the work was not completed.

In another experiment measurements were made of the changes in contact potential and electron emission when the temperature of a tungsten filament was varied, thereby changing the amount of caesium adsorbed on its surface. The experimental tube was similar to those described above, and had two filaments 15 cm long and 0.0102 cm diameter. One filament was of thoriated tungsten, and the other of pure tungsten. The area of that part of each of the filaments inside cylinder *C* (Fig. 1) was 0.30 cm². The thoriated filament was activated, and held at a constant temperature as the source of electrons. The caesium in the tube was kept at room temperature. Cylinder *C* was kept at -1.3 volts with respect to the negative ends of the filaments during the contact potential measurements.

The tungsten filament was heated to the temperatures shown in the first column of Table III. These temperatures are those calculated from the heating currents, and are subject to two large sources of error—cooling by the leads, and heating by radiation from the other filament. From rough calculations it appeared that these errors, although of the order of 100° at the lowest temperatures, approximately compensated each other in the center part of

⁵ Kingdon, Phys. Rev. **24**, 510 (1924).

⁶ Dushman and Ewald, Phys. Rev. **29**, 857 (1927).

⁷ Dushman, Phys. Rev. **21**, 623 (1923); **25**, 338 (1925).

the filament, so that the original temperatures as determined from the heating current have been retained in the table.

TABLE III.

T °K	i_{obs} μa	V_f volts	ΔV volts	$\Delta\phi$ volts	ϕ volts	b degrees	i_{calc} μa
542	0.87	0.13	-0.565	-0.50	[1.38]	[16000]	[0.87]
607	7.39	0.21	-0.520	-0.42	1.46	16930	5.2
645	7.80	0.26	-0.465	-0.33	1.55	17980	6.2
678	5.80	0.31	-0.395	-0.24	1.64	19020	5.4
741	1.83	0.42	-0.190	+0.02	1.90	22030	1.3
794	0.41	0.55	0.000	0.27	2.15	24950	0.29
846	0.10	0.68	+0.190	0.53	2.41	27950	0.063
891	0.027	0.83	0.330	0.74	2.62	30400	0.023

The electron emission from the caesiated filament is given in the column headed i_{obs} (cylinder C was of course made positive for the emission measurement). The emission at first rose as the temperature was raised, but decreased at the higher temperatures, since some of the caesium coating had been driven off. At each temperature the rates of adsorption and evaporation of caesium were in equilibrium. V_f denotes the voltage drop over the caesiated filament due to the heating current. At each filament temperature the voltage ΔV was determined at which the caesiated filament must be held with respect to the thoriated filament in order that the former should receive $0.5 \mu a$ electron current from the latter. This current flow was also affected by the potential drop over the caesiated filament, and in order to correct approximately for this, $1/2 V_f$ was added to ΔV , the sum being given in the column headed $\Delta\phi$. These values of $\Delta\phi$ then show the changes in the work function as the amount of caesium on the surface was varied, but do not fix its absolute value at any point. If the filament had been heated hot enough to keep its surface free of caesium, and thus fix ϕ from the value for tungsten, other complicating effects would have been introduced. The only available method for fixing the scale of ϕ was from the observed electron emission, using the emission equation

$$i = 60T^2 e^{-b/T} \text{ amps. per cm}^2. \quad (2)$$

From this we find that at the 542°K point $b = 16000^\circ$ and hence $\phi = 1.38$ volts. The other values of b and ϕ given in Table III were determined from this base value and the values of $\Delta\phi$. The last column of the table gives values of the emission from the caesiated filament calculated from Eq. (2) and the values of ϕ . The observed and calculated values of the emission agree fairly well.

Too much emphasis must not be placed on this agreement for the following reasons:—(1) the uncertainty in the temperature scale caused by lead cooling and radiation from the thoriated filament, (2) the approximate nature of the correction to ΔV involving V_f , and (3) the fact that the constant 60 in Eq. (2) is not correct for most adsorbed films. These inaccuracies are not inherent in the method, but could be overcome by changes in the construction of the tube so as to reduce the error in filament temperature; and by changes in the experimental procedure, so as to eliminate or correct for the effect of V_f , and to enable a direct calibration of the scale of ϕ to be made from the value for pure tungsten.