# The Contact Difference of Potential Between Tungsten and Barium. The External Work Function of Barium

PAUL A. ANDERSON, *State College of Washington*

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An intensive study of the contact difference of potential between tungsten and barium has been made with the purpose of developing a generally applicable method of measuring contact potential differences under the most rigorous conditions possible. Extreme outgassing of surfaces in the highest attainable vacuum is found to be essential but when these requirements are met highly reproducible measurements can be obtained. The tubes are sealed from the pumps after baking, gettered with barium, and immersed in liquid air during measurement. The tungsten, in the form of a thin ribbon, is cleaned by flashing at 2800°K until its work function remains unaltered by further heating. Barium films are deposited on the tungsten ribbon by thermal vaporization and their reproducibility checked by measuring a succession of films formed in a fractional distillation of the metal. The measuring technique is designed to detect any changes in work function which may occur immediately after the preparation of a clean surface and to prevent accidental contamination of those parts of the tube which must be maintained at constant work function. Sharp localization of the surface areas for which electron current-potential characteristics are taken and an increased sensitivity of measurement are secured by using a narrow and intense beam of electrons and determining displacements of the characteristics in the retarding potential region. Measurements with three types of tubes and with samples of tungsten and barium from several different sources give the value $2.13\pm0.05$ volts for the contact difference of potential between tungsten and barium; $2.39\pm0.05$ equivalent volts for the external work function of barium. The method can, presumably, be quite generally applied to the measurement of the contact potential difference between a tungsten reference surface and any other metal and is adapted, also, to the study of dilute films of any metal on tungsten.

IT is a consequence of the Sommerfeld theory that the contact difference of potential between two metal surfaces is equal to the difference between their external work functions:[1]

$$V_{ab}=\phi_a-\phi_b.$$

Contact potential measurements should be capable (1) of determining work function values for a far wider range of surfaces than can be studied by either thermionic or photoelectric methods, and (2) of furnishing a powerful means of attack upon adsorption problems, in which studies of highly dilute adsorbed films may be expected to be especially significant.

The fact that these rather attractive possibilities have not been more fully realized in practice probably can be attributed to the lack of a generally applicable technique of measurement providing for adequate vacuum conditions and sufficiently thorough outgassing of surfaces. This lack, evident even in much of the recently published work, is reflected in the discordant results which have characterized contact potential measurements generally. It was the purpose of the present work to make a careful study of contact potential in a single system of intrinsic importance with a view to determining the vacuum and outgassing conditions required for reproducible measurements, and to developing a method of measurement applicable to a wide variety of metals.

The main features of the method as it has been worked out are: (1) After thorough outgassing the tube is sealed from the pumping system, gettered by the vaporization of barium, and immersed in liquid air during measurement. (2) Clean tungsten is chosen as a reference surface to which the contact potential difference of the pair of metals is referred. For the purpose of systematizing the results of different investigations the selection of a standard reference surface has manifest advantages. Since tungsten is one of the few metals which can be heated to temperatures necessary for the removal of all gaseous and solid surface impurities and since its work function is known so accurately that a reliable determination of the contact potential between it and any "unknown" surface establishes the work function of the latter, it is well suited to the purpose. (3) The metal surface to be measured against tungsten is formed by thermally vaporizing the metal and the purity of the film

[1] Eckart, Zeits. f. Physik **47**, 38 (1928).

finally measured checked by measuring the contact potential of each of a succession of films formed in a fractional distillation of the metal. The attainment of a contact potential unaltered by further distillation is taken as the criterion of a clean film. It is likely that the metals which melt or vaporize at temperatures below the vaporizing temperatures of the common oxides and salts, i.e., most of the common metals, can be freed of solid surface impurities as well as adsorbed gases only by such a distillation in high vacuum. The extension of the technique to the general case in which barium is not one of the metal pair undergoing measurement involves merely the addition of a separate barium gettering chamber to the tube. (4) A method of measurement is used which makes it possible to follow closely any changes in work function which may be experienced by the tungsten immediately after it is flashed, or by the freshly distilled metal film immediately after it is formed. It was found early in the course of this work that in an unsatisfactory vacuum the work function of a fresh surface changes very rapidly and may then attain a constant value which, without provision for immediate measurement, might be accepted as characteristic of the clean surface.

## METHOD

Contact differences of potential have been measured in the past by the well-known Kelvin method[2] and by determining the displacement along the potential axis between the parallel electron current-potential characteristics given by surfaces of different work function. The latter method has been employed in various modifications by Mönch,[3] Langmuir and Kingdon,[4] and Kösters,[5] and Mönch[6] has published some results which seem to indicate that the Kelvin and electron methods when applied to a given surface yield values which agree within the experimental error.[7]

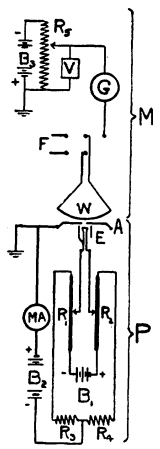


FIG. 1. The circuits: $P$ for producing electron beam and $M$ for determining electron current-potential characteristics of the surface $W$. $R_1=R_2=1.2$ ohms. $R_3=R_4=300$ ohms. $F$ = flashing current leads.

In the present work the electron method as previously employed has been modified by using, instead of a diffuse stream or space-charge cloud of electrons spread over a relatively large area of the receiving surface, an intense and narrow beam of slow electrons projected against a small and sharply defined section of the surface. This area, while large with respect to the small-scale structural variations which characterize the surface, is small enough to eliminate uncertainties due to accidental large-scale variations over the surface. The sensitivity of measurement, as determined by the slope of the electron current-potential characteristic, is also materially increased. By using the characteristic curve displacement in the region of retarding potential it has been possible to obtain with a short period galvanometer of only moderate sensitivity ($10^{-8}$ amp.) a precision of measurement of the order of $10^{-3}$–$10^{-4}$ volt, or from ten to one hundred times the best reproducibility which can be expected. Fig. 1 is a self-explanatory diagram of the electrical circuits with a schematic indication of the tube.

The method of measurement may be outlined as follows. A beam of 4 to 8 volt electrons is directed by the electron gun $EA$ against a small area near the center of the strip of tungsten foil $W$ and the current to the foil plotted as a func-

[2] An interesting modification of the Kelvin method has been described by Zisman, Rev. Sci. Inst. **3**, 367 (1932).
[3] Mönch, Zeits. f. Physik **47**, 522 (1928).
[4] Langmuir and Kingdon, Phys. Rev. **34**, 129 (1929).
[5] Kösters, Zeits. f. Physik **66**, 807 (1930).
[6] Mönch, Zeits. f. Physik **65**, 233 (1930).
[7] It should be pointed out that it is only in the work of Langmuir and Kingdon that the outgassing methods employed have been adequate. Their technique is adapted only to the study of surface films of substances which have an appreciable vapor pressure at room or slightly elevated temperatures.

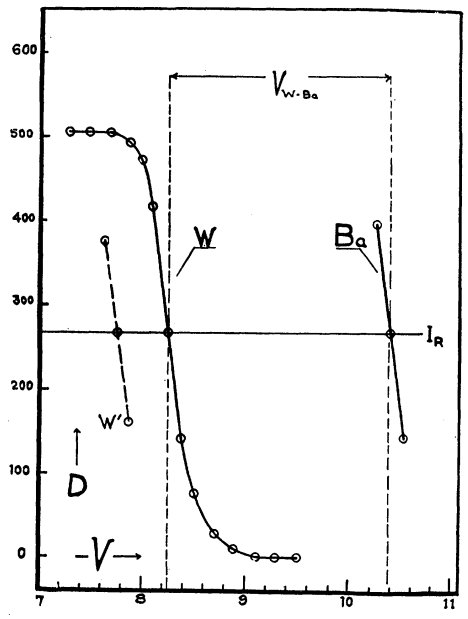


FIG. 2. Typical current-potential characteristics for clean tungsten *W*, barium *Ba*, and incompletely cleaned tungsten *W'* surfaces. Current in mm galvanometer deflection *D* Retarding potential $-V$ in volts. 7 volt electrons.

tion of the retarding potential applied to the strip. A typical curve is reproduced in Fig. 2. Any change in the work function of the surface, whether due to a readsorption of gas or to the deposition of another metal, produces a shift of the straight-line portion of the curve by an amount equal to the contact difference of potential between the initial and final states of the surface. The shifts produced by a barium coating and by a slight gas contamination are indicated in the figure. In practice the shift is determined by first plotting the curve for the clean tungsten reference surface, choosing a reference current $I_R$ near the middle of the straight-line part of the curve, and then determining the change in applied potential necessary to reestablish this reference current. Rapid changes in work function such as occur immediately after flashing tungsten in an unsatisfactory vacuum are followed by observing the drift in the galvanometer deflection for a fixed applied potential. In an adequate vacuum this drift becomes negligible during the time required for a set of measurements.

In the early stages of the work an ionization manometer was used for measurement of residual gas pressures in the tube but it became clear that the testing procedure just outlined, referred to hereafter as the "vacuum test," was more reliable than measurements with the ionization gauge, which itself usually evolves or cleans up gas during operation. Such ionization gauge measurements as were made showed the pressure to be $10^{-8}$ mm or less when the vacuum test was satisfactory.

Photoelectric emission from *W* under the stimulus of light from the electron emitter was a possible source of error which had to be considered. An inverse electron current large enough to introduce such an error would, however, produce a detectable overrunning of the galvanometer zero at high retarding potentials. Since no overrunning could be detected either with tungsten or with barium surfaces the inverse currents if present must have been negligibly small.

## THE TUBE

Tubes of three different types, only one of which will be described in detail, have been studied during the course of this work. The first tubes to be tried out, designated Type 1, were of very simple design. The tungsten strip was mounted opposite the mouth of an electron gun of the Farnsworth pattern[8] and barium vaporized from a molybdenum foil oven mounted at the side of the tube between gun and strip. After outgassing, sealing off, gettering, and prolonged immersion of the tube under liquid air or liquid hydrogen[9] the vacuum was such that the galvanometer deflection read a few seconds after flashing the tungsten at 2800°K remained unchanged to within 1 mm when the tungsten was allowed to stand cold for periods as long as 20 minutes; i.e., the work function remained constant to within 0.001 volt during this period. The behavior of a freshly deposited barium film was similar, but upon removing the barium by flashing and repeating the measurements, or carrying through measurements on successively deposited films, erratic variations in the contact potential differences amounting to several decivolts were found.

[8] Farnsworth, J. O. S. A. and Rev. Sci. Inst. **15**, 290 (1927).

[9] This part of the work was carried out at the Kältelaboratorium of the P. T. R., Berlin, during the tenure of a National Research Fellowship.

These variations were attributed, correctly as later work showed, to contamination of the electron gun with barium, which apparently migrated over the outside of the oven and was vaporized from its bottom. As would be expected, the variations between successive measurements decreased as repeated contaminations brought the gun surfaces nearer to an equilibrium state, and in fact the contact potential value finally obtained with this type of tube agrees to within 0.1 volt with our latest value.

It was clearly desirable, however, to devise a tube in which all possibility of contamination of parts which must remain at constant work function is eliminated. The later tubes were, therefore, designed to meet the following specific requirements. (1) During deposition of barium or other metal on the tungsten surface it must be impossible for the vapor to come into contact with any part of the electron gun. (2) It must be possible to fuse and vaporize the metal in the oven while access of vapor to the tungsten is prevented and then, without cooling the oven, to form the film which is to be measured. (3) It must be possible to remove the metal film from the tungsten without permitting the vapor to strike the gun. (4) The tungsten receiving strip must be close enough to the mouth of the electron gun during the measurements to insure the localization of the beam at a small spot near the middle of the strip. Of these requirements the first is essential in any measurement, the second is added to eliminate the possibility of forming the film while the vaporizing metal is emitting gas which it has absorbed while standing cold, the third to allow of repeating the measurements under constant conditions, and the fourth to eliminate errors due to electrons picked up by lead wires or the less thoroughly outgassed ends of the receiving strip. Other necessary features of a satisfactory design are the elimination of large metal parts which cannot be thoroughly outgassed and sufficient compactness to permit of immersing the tube under liquid air.

The tube used in our latest measurements is sketched in plan and elevation in Fig. 3. The requirements noted above are met by placing the tungsten ribbon $W$ on a simple rotating spindle $S$ and by suitable geometric arrangement of the electron gun $EA$, vaporizing oven $B$, and mica shield $P$.[10] The spindle was built of two lengths of 1.5 mm tungsten wire connected by a Pyrex bead as shown, and a length of close-fitting Pyrex capillary which carried the shield, glass-enclosed armature $I$, and glass sights $T$. The spindle was mounted on small nickel sockets pressed on the 1.5 mm tungsten leads which supplied the flashing current to the strip, and driven by the action of a small electromagnet on $I$. Any desired setting of the spindle could be easily obtained to

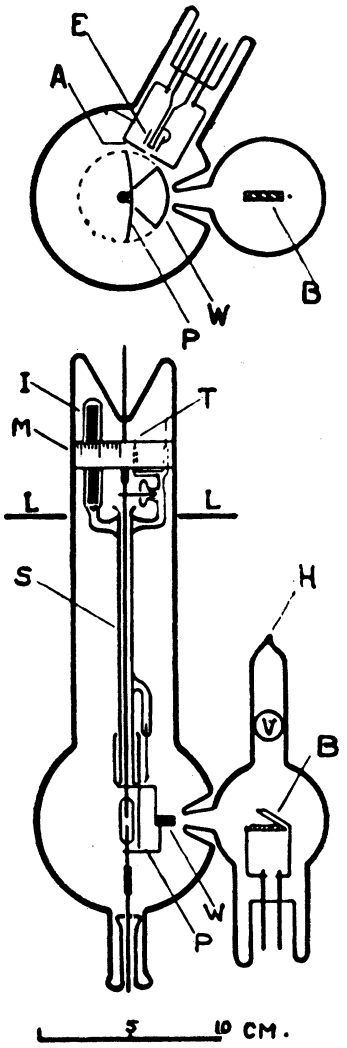


FIG. 3. The tube. $W$ = tungsten ribbon. $B$ = barium oven. $EA$ = electron gun. $S$ = rotating spindle.

[10] A glass or quartz shield would be preferable. The mica was badly blistered by the heat radiated from the tungsten ribbon during flashing.

$\pm 0.25$ mm by sighting across the paper scale $M$, pasted on the outside of the tube, and the sharp-pointed glass sights. During measurement the tube was immersed in liquid air to the level $LL$. The shield $P$, which became coated with barium during the measurements, was grounded through a whisker which connected the light molybdenum wire supporting the shield with the walls of the tube, which were in turn connected by another whisker to the grounded anode of the electron gun. The spindle sheath was petticoated as shown to preserve the insulation between the leads to $W$ and ground.

The vaporizing oven $B$ was of 0.01 mm molybdenum foil 5 mm wide, bent to form a shallow trough in its horizontal section and carried up to form a heated deflector, which directed an adequate quantity of barium vapor toward the orifice. The oven and orifice defined the vapor beam which entered the main chamber and it is clear that all of the requirements mentioned above could be satisfied by appropriate settings of the spindle. The electron gun consisted of the emitter $E$ of tungsten foil $0.02\times 2\times 8$ mm bent into a narrow stirrup with effective emitting surface $2\times 2$ mm, a focusing cylinder made of foil of the same thickness and welded to the negative emitter lead, and the accelerating diaphragm $A$, a strip of pure tungsten foil $0.01\times 10\times 30$ mm mounted on 1.5 mm current leads. The hole at the center of $A$ was 1.2 mm in diameter. The field set up by the anode and focusing cylinder concentrated the electrons from the emitter upon the center of the anode near the orifice, increased the electron beam intensity and the slope of the current-potential curves, and prevented the straying of electrons around the edges of the anode. The construction of the anode allowed it to be cleaned by flashing not only during the outgassing period but at any time during the course of the measurements.

The tungsten ribbon $W$, $0.025\times 4\times 30$ mm, was cut from foil which was stated by the makers, the P. R. Mallory Company, to be the purest available. It, as well as the emitter, anode, and oven, was attached to its molybdenum support wires with small molybdenum rivets to prevent contamination of the surfaces by migrating welding flux.

## Procedure

During outgassing the tube was connected at $V$ with a conventional pumping system which consisted of, numbering from the tube, two liquid air traps in series, $CO_2$ trap, McLeod gauge, and Gaede two-stage mercury diffusion pump. There were, of course, no waxed or greased joints between pump and tube. The liquid air trap nearest the tube showed no trace of condensed mercury at any time. Before the barium was put into the oven the tube was baked at 500°C for at least 48 hours and the metal parts given a preliminary heating. The tube was then opened at $H$, about 1.5 grams of barium placed in the oven, and the tube quickly sealed off and evacuated. Barium from two sources was used in the measurements, a sample prepared originally by Dr. A. J. King and furnished to me by Professor P. W. Bridgman with an analysis showing a trace of strontium as the only impurity, and a sample obtained from Osram which was stated to contain traces of strontium and iron as the only impurities. No differences between the samples were detected in the measurements.

After re-evacuation the oven was glowed and the barium melted down thoroughly. The tube was then baked again for at least 60 hours at 350°C (a slow distillation of barium which destroys the insulation in the tube seems to occur at 500°) and all of the tungsten strips flashed intermittently, $A$ at about 1600°K, $E$ at 2200, and $W$ at 2200 with occasional short flashes at 2800. The glowing temperatures were determined to sufficiently close approximation by making an initial rough calibration of the readings of an optical pyrometer against heating currents for each of the strips. During these treatments the molybdenum support wires became white hot and the tungsten leads themselves probably were heated sufficiently to effect a superficial outgassing of their surfaces. The tube was sealed from the pumps while still hot and a fresh coat of barium immediately deposited on the walls of the oven chamber.

The final cleaning of the tungsten ribbon $W$ was accomplished after sealing off and immersing the tube in liquid air, and the progress of this cleaning followed by taking the current-potential characteristics for the strip after successive flash-

ings. A new heating current-temperature calibration was made for $W$ through an uncoated section of the Dewar cylinder. The strip was given repeated flashings at 2800°K and accepted as clean only after the potential setting for a given reference current remained unchanged by each of several successive flashings. During this cleaning process fresh barium coatings were periodically deposited on the oven chamber walls and the vacuum test applied to check the vacuum conditions in the tube.

The general features of the measuring procedure have been described above. After obtaining the potential setting for the clean tungsten surface, $W$ was turned into the barium vapor jet and immediately after a film had been deposited swung in front of the electron gun. The setting of the sights was such that the electron beam was centered on the deposit; it was also the same as in the preceding measurement on clean tungsten to insure an equivalent geometric arrangement in the two measurements. After the applied potential had been altered to reestablish the reference deflection this deflection was watched for drift, which would indicate a progressive change in the work function of the fresh film. We were surprised to find that these barium films were actually more stable than the freshly cleaned tungsten surfaces. In practically all cases the work function of a fresh barium film remained constant to within a few millivolts for periods of at least 20 or 30 minutes and continuation of the observations on a single film for an hour or more has failed to discover variations greater than this. Since these variations were fluctuations rather than progressive drifts they probably originated in the measuring circuit or emitter rather than in the film. After determining the correct setting for the first film a succession of fresh films was formed and each measured immediately after being deposited. Presumably due to the fact that the barium had been melted repeatedly during the gettering and a considerable fraction of it vaporized no progressive change in work function was found even in the first sequence of films to be formed and the measurements on these films were highly reproducible throughout a complete set of determinations in which as many as 22 different films were measured. Repeated checks to within a few millivolts could be obtained and the appearance of larger variations could be accepted as a reliable indication of a change in electron emission from the gun. After establishing the potential setting for barium and thus completing one determination of contact potential difference the barium film was removed by flashing the strip and the whole measuring procedure repeated. As many as eight such determinations could be made before the tungsten strip burned out.

Great care was taken to hold the total electron emission of the gun constant during a series of determinations. The filament battery was made up of six 100 ampere hour accumulators of similar discharge history in parallel, the sliding contacts of the rough-adjustment 1.2 ohm rheostats (Fig. 1) were replaced by screw clamps, and fine regulation of the emitter heating current accomplished by a heavy alloy rod moving in a mercury well. The total electron current was checked frequently and adjusted if necessary.

## Results

Table I is a resumé of the measurements made with the final tube, Type 3, together with the value obtained with the Type 1 tube (which as mentioned above was not regarded as entirely reliable at the time it was made) and two measurements made with the Type 2 tube, which was somewhat similar in design to the Type 3. Only the two measurements recorded were made with the Type 2 tube before the tungsten ribbon, which had been given an excessive heat treatment, burned out. The measurements, with the exception of the two differentiated with aster-

TABLE I. *Measurements of the contact difference of potential between tungsten and barium.* Accepted value: 2.13 volts.

| Cell type | $(-V)$ W | $(-V)$ Ba | Contact potential |
|---|---|---|---|
| 3 | 7.70 | 10.30 | 2.60* |
| 3 | 7.90 | 10.30 | 2.40* |
| 3 | 8.16 | 10.30 | 2.14 |
| 3 | 8.15 | 10.30 | 2.15 |
| 3 | 8.15 | 10.30 | 2.15 |
| 3 | 8.17 | 10.30 | 2.13 |
| 3 | 8.19 | 10.30 | 2.11 |
| 3 | 8.18 | 10.30 | 2.12 |
| 1 | 2.30 | 4.52 | 2.22 |
| 2 | 7.99 | 10.10 | 2.11 |
| 2 | 8.09 | 10.17 | 2.08 |

isks, group closely about the value 2.13 volts. Examination of the potential settings shows that the two high values originate in abnormally high work function states of the tungsten surface. Since the adsorption of any of the gases which are likely to be present in a tube raises the work function of clean tungsten[11] these high values have been disregarded and $2.13\pm0.05$ volts chosen as the value to be considered representative of these measurements. If the work function of clean tungsten is taken as 4.52 equivalent volts[12] the external work function of barium obtained by application of the Sommerfeld relation is $2.39\pm0.05$ equivalent volts.

The photoelectric measurements of Pohl and Pringsheim[13] made on barium which was not outgassed indicated a "threshold" between 1.7 and 2.3 volts. Since the presence of gas generally lowers the work functions of the electropositive metals and correction of an apparent threshold to its true value at 0°K leads to a higher work function value, the true value for barium would be expected to be near or above Pohl and Pringsheim's upper limit of 2.3 volts. Nelson[14] has measured the contact difference of potential between tungsten and barium-coated tungsten emitters incidentally to a study of their thermionic properties. He reports a value of 2.8–2.9 volts, which corresponds in order of magnitude to measurements taken in the present work between barium and tungsten surfaces which had not been completely cleaned. Nelson gives few details of the outgassing treatment to which he subjected the metal parts of his tube. Since these parts were very closely spaced, heating of the anode, oxide-coated filaments, and collector by radiation from the emitter might have caused them to give up gas during the measurements. The barium was supplied by evaporation from oxide-coated filaments and there is the additional possibility that the electrolysis of the oxide may have been accompanied by a slight evolution of oxygen. In view of the tendency of impurities to decrease the work functions of the electropositive metals and, especially, of the difficulty of freeing a tungsten surface from the oxygen coating which raises its work function, it seems probable that the true value of the contact difference of potential W-Ba is at least as low as the value found in the present work.

By adjusting the temperature of the barium oven to give a low rate of vaporization and limiting the time of exposure of the tungsten ribbon to the vapor jet we have found it possible to prepare and measure dilute films of barium on tungsten (covering factor $\theta$ of the order of unity and less). As would be expected from the results of thermionic measurements[15] the work function of the composite surface decreases with increasing coverage to a minimum and then increases to the value characteristic of pure barium. The results of these measurements will be reported in detail in a later communication, together with results for barium films on silver and gold. The interpretation of such measurements is a problem quite distinct from that involved in contact potential measurements on pure metals and it is desirable that considerably more data which can be compared with existing photoelectric and thermionic measurements be obtained before an interpretation is attempted.

I should like to thank Dr. W. Meissner and Former President Paschen of the Reichsanstalt for their kindness in granting me the facilities of their laboratories, where the first part of this work was carried out.

[11] Langmuir, J. Am. Chem. Soc. **38**, 2221 (1916); Warner, Proc. Nat. Acad. Sci. **13**, 56 (1927).
[12] Dushman, Rowe, Ewald and Kidner, Phys. Rev. **25**, 338 (1925).
[13] Pohl and Pringsheim, Verh. d. Deutsch. Phys. Ges. **13**, 474 (1911); Hughes and DuBridge, *Photoelectric Phenomena*, p. 75.
[14] Nelson, Physics **1**, 84 (1931).
[15] Langmuir and Kingdon, Phys. Rev. **24**, 510 (1924); J. A. Becker, Phys. Rev. **28**, 341 (1926).