these configurations. At most five of the twelve levels are observed, and not even the J values of these are certain.⁵ It may be that the above formulas can be of use in interpreting these observations. Perhaps the five observed levels, four lower and one upper, are at the positions of the five collapsed levels given by these formulas. On the other hand, the J=2 levels may be displaced from these positions because of a non-negligible G_2 value. One would not expect G_4 and ζ_f to be large enough to give significant departures for the levels of other Jvalues. If we attempt to fit the four lower observed levels by means of the above formulas we obtain the results of Fig. 2. The level Wwhich is observed to have the J value 4 or 3 may well be a double 4 and 3 level. The level Yis observed to be 1 or 2. No J=1 is expected in this vicinity so this is probably J=2, with a J=3 nearby. The level U is observed as 4 or 3. It is probably 4 with a J=5 nearby. The level X is definitely observed as J=1. A level of J=2should be near. The single observed upper level is listed as J=1 or 2. It cannot be J=1 since there is no level in the upper group with J=1. This upper level is observed only for 4f, 5f, and



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6f. Fig. 2 indicates fairly large perturbations of these two configurations which are expected since the lower group of 5f is overlapped by 6pand the upper group of 5f is close to the lower of 6f. Nevertheless, the ζ_p values obtained from the position of the upper J=2 level according to the above formulas—955.0 cm⁻¹ for both 5f and 6f—agree well with the value 954 from the A II ${}^{2}P$ splitting. For $2p{}^{5}4f$ only X, Y, and the upper J=2 are observed. The ζ_p value calculated from the above formulas for these is 955.24 cm⁻¹, which checks in this case also the interpretation which we have given.

The Contact Difference of Potential Between Barium and Magnesium

PHYSICAL REVIEW

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With the purpose of subjecting the electronic method of contact potential measurement to a thorough test for consistency with independent photoelectric work function determinations, the Volta potential Ba-Mg has been measured for some 30 pairs of surfaces and the results compared with recent careful photoelectric studies of these metals. Each surface was prepared by fractionally distilling the metal in a gettered vacuum and revaporizing a middle fraction to form a thick film on glass at room temperature. Each film was measured a few seconds after deposition and tubes of two different designs used to minimize the possibility of errors originating in tube geometry. The majority of the observed Volta potentials fell within the range of values predicted by the photo-

 $\mathbf{I}_{\text{work functions of barium by Jamison and}}^{N}$

electric data, 1.08–1.16 v, and no values below this range were found. The magnesium films were largely responsible for variations in the Volta potential and a few gave potential settings sufficiently low (work functions sufficiently high) to raise the observed Volta potentials to a maximum of 1.26 v. Since all probable contaminations should lower the work function the maximum value is regarded as the most reliable. Assuming a work function of 2.52 ev for Ba this gives 3.78 ev for the work function of Mg. Observations on the optical reflection of the magnesium surfaces suggest, however, that a work function of 3.65 ± 0.05 ev may be characteristic of mirror-like surfaces of the metal; 3.78 ev of macrocrystalline (matte) surfaces.

Cashman¹ and of magnesium by Cashman and $\overline{}^{1}$ Jamison and Cashman, Phys. Rev. 50, 624 (1936).

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FIG. 1. Type 1 tube. First A and second B vaporizers of 0.025 mm Mo foil 8 mm wide attached to 3-lead stem with Mo rivets; one of 60 mil leads common. Films formed on Pyrex drum R were moved into reproducible positions before electron gun E by armature M and glass sights T, set on an external paper scale. Contact with films established by Pt wire embedded in R and welded to 20 mil tungsten wire brush K. Gun of 4 mil Ta foil; emitter 1 mil tungsten foil 1.5 mm wide. The second vaporizing chamber, not shown, was identical in design with the first.

Huxford,² and Mann and DuBridge³ the method of preparing the metal surfaces has been similar

to the fractional distillation method employed by the author in Volta potential measurements on tungsten-barium⁴ and barium-silver⁵ but supplemented by multiple vaporization of the middle fractions. These photoelectric studies must be regarded as among the most reliable yet made for any of the metals and the standardization of a satisfactory technique for preparing surfaces offers the possibility of testing under unusually favorable conditions the consistency of work function determinations by the photoelectric and Volta potential methods. In several instances checks of this relation, $V_{ab} = \phi_b - \phi_a$ (Sommerfeld-Eckart equation), have been reported but generally either the photoelectric or contact potential measurements, or both, have been obtained under questionable experimental conditions.

It was the purpose of the present work to make a careful study of the contact difference of potential between surfaces of barium and magnesium each prepared by fractional distillation and revaporization of the middle fraction and to compare these measurements with the photoelectric data. Since there is now abundant evidence to show that work functions are structure dependent, the barium and magnesium films were formed on glass at room temperature as in the photoelectric investigations rather than at liquid-air temperature as in our previous Volta potential studies. To minimize the possibility of undetected errors originating in tube geometry the measurements were made with tubes of two different designs.

METHOD. THE TUBES

The method of measurement, based on the determination of the shift of an electron currentretarding potential characteristic with change of work function, was that employed in previous studies.^{4, 5} The scheme of preparing the metal surfaces and bringing them into the measuring position involved, in both types of tubes and for each of the metals: (1) vaporization and rejection, for other than gettering purposes, of the first half of the original sample, (2) collection on a second vaporizer of the middle fraction of metal distilled from the first vaporizing oven, (3) revaporization of this selected fraction to

² Cashman and Huxford, Phys. Rev. 48, 734 (1935).

³ Mann and DuBridge, Phys. Rev. 51, 120 (1937).

⁴ P. A. Anderson, Phys. Rev. 47, 958 (1935).

⁵ P. A. Anderson, Phys. Rev. 49, 320 (1936).

form a thick film of the metal on a clean glass surface, and (4) provision for displacement of the freshly deposited film to a reproducible position in which it was centered before an electron gun. The tubes used in the first measurements were designed originally for work under liquid air and the movable glass receiver was a drum carried on a vertical glass spindle, Fig. 1. In the second type of tube, Fig. 2, alternate layers of barium and magnesium were deposited on a glass disk moved by magnetic control along a double glass rod track, which extended across both vaporizing chambers and the electron gun. The essential constructional details are indicated in the legends of the figures.

MATERIALS

The magnesium was a sample of extremely high purity kindly furnished to me by Dr. Cashman and taken from the stock used by him in his photoelectric measurements. The barium, from the stock used in our previous contact potential work, was obtained from Osram and contained traces of iron as the only important impurity. As compared to samples which have been secured from other sources this barium is relatively ductile and free from absorbed gas.

PROCEDURE

The outgassing procedure was similar to that described in previous reports except that a new high frequency bombarder has made it possible to push the heating of the metal parts to temperatures limited only by the vaporization of the tantalum. In order to eliminate the cost of liquid air, one of the tubes was pumped on an oil diffusion system and protected by two longcolumn charcoal traps in series. These traps were of a new design⁶ which permits heating the charcoal to incandescence in an all-Pyrex system. The behavior of this tube was indistinguishable from that of the others which were pumped with mercury vapor and protected by double liquidair traps.

After outgassing of the glass and metal parts and before seal-off the barium was melted down several times on the first vaporizing oven and a considerable fraction of it vaporized. The magnesium was treated similarly but usually could be only partially fused before a third or more of it vaporized. After seal-off the melting of the barium and vaporization of further fractions of barium and magnesium were repeated several times and the second vaporizers flashed to remove all of the first condensates. During these preliminary treatments the glass drum of the type 1 tubes was always turned into the "dumping position;" the deposits formed by direct distillation from the first vaporizers and by discarded fractions from the second vaporizers were confined to one spot on the drum while the remainder of its surface remained uncoated until the measured films were laid down. In the case of the type 2 tubes the glass disk was moved into the appropriate vaporizing chamber only when the final distillations from a second vaporizer were to be made. The first vaporization of the middle fraction of each metal was carried out at an oven temperature just sufficient to form in one to two hours on the second vaporizer a deposit adequate for the preparation of several successive fresh surfaces on the glass receiver. The initial measurement on a film was made within a few seconds of completing the final deposition and the potential settings for fixed reference current followed closely during the early history of the film. The possibility of thus detecting and following work function changes which may occur immediately after the formation of a film is one of the most useful characteristics of the method. With a negative potential on the film, i.e., under the conditions of measurement, sunlight incident



FIG. 2. Type 2 tube. First and second vaporizers, A and B, and electron gun E as in type 1 tube. Contact to films by Pt wire embedded in edge of 2 cm Pyrex disk R, 20 mil tungsten wire brush K and 10 mil tungsten wire spring C (rotated 90° in sketch). Tube flattened at F to prevent vapor exchange. R moved under gun during first vaporizations to protect it from contamination. Setting of slide determined by paper scale on armature tube.

⁶ P. A. Anderson, Rev. Sci. Inst. 8, 493 (1937).

on the tube was found to generate a large photoelectric emission from film to gun and all the measurements were carried out in a shuttered room. No detectable emission was produced by ordinary artificial light or by the light from the emitter filament. The potential applied to accelerate the electrons in the gun was 10.01 v throughout the measurements and galvanometer deflections for zero potential on the film were of the order of 950 mm. The reference deflection was 500 mm and the retarding potentials required to establish this deflection were, in a typical measurement, 10.82 v for magnesium and 12.00 v for barium. The sensitivity of measurement in terms of change in deflection per volt change in applied potential, or work function, was of the order of 1500 mm/volt. The energy of the significant fraction of the electrons collected by the film at the reference setting was a small fraction of one volt and secondary emission must have been negligible.

THE VOLTA POTENTIAL Ba-Mg

Of the several hundred measurements made on more than 30 pairs of films the majority gave Volta potentials within the range predicted by Jamison and Cashman's photoelectric value for the work function of barium,¹ 2.52 ev, and the Mann and DuBridge³ value for magnesium, 3.68 ev. The first series of measurements made with a type 1 tube gave reproducible Volta potentials of 1.08 v in exact agreement with the above mentioned value for barium and Cashman and Huxford's² value for magnesium, 3.60 ev, but in the later series most of the observations were grouped in the range 1.15-1.19 v. In several instances higher values were recorded and one pair of films gave a Volta potential of 1.26 v, the maximum value observed. Throughout the measurements the potential settings for fixed reference current were highly reproducible for the barium films and the Volta potential Ba-Ba taken on successively deposited barium surfaces was always found to be zero to ± 0.01 v whenever it was checked. Since no systematic trend in the measurements with change of tube design or between different series of observations with tubes of the same design could be detected, the variations in Volta potential apparently origi-

nated in variations between the individual magnesium surfaces. A possible clue to these variations is given by the observation that a fresh mirror-like surface of magnesium deposited on the virgin glass disk of a type 2 tube gave a Volta potential of 1.16 v against a barium film laid down upon it but as successive alternating films of the metals were deposited the magnesium surfaces took on the diffuse reflection characteristic of a finely polycrystalline metal while the Volta potential increased to 1.24 v. If residual gas was responsible for these variations it must be concluded that magnesium is sensitive to concentrations of gas which leave barium films in the same tube entirely unaffected. In tests for change of work function with aging none of the barium films studied showed a drift measurable within 72 hours. The magnesium films were somewhat less stable and in several instances exhibited drifts of 0.02-0.05 v toward lower work function within a few hours of deposition. These drifts were not, however, progressive and no changes greater than 0.05 v could be detected within 72 hours.

THE WORK FUNCTION OF BARIUM

Since the value assigned to the work function of magnesium by this method depends directly upon the work function of barium, the selection of the most probable value for ϕ_{Ba} becomes of first importance. The unique advantages of barium as a reference metal lend a more general significance to such a selection. In the first of this series of contact potential studies⁴ the Volta potential W-Ba was found to be 2.13 ± 0.05 v at liquid-air temperature and a value of 2.39 ± 0.05 ev was computed for ϕ_{Ba} at this temperature on the assumption that the work function of tungsten at 90°K is equal to 4.52 ev, the thermionically determined "heat function." This assumption, justified only because of our lack of information regarding the temperature coefficient of the work function of tungsten, is an approximation at best and subsequent investigations, in particular the photoelectric work of Jamison and Cashman on barium, make re-examination of our earlier value desirable. Reimann,7 assuming zero reflection coefficient and a roughness factor of 1.3,

⁷ Reimann, Phil. Mag. 20, 594 (1935).

has computed ϕ_W to be 4.64 ev at 1500°K. More recently the same author⁸ has obtained measurements yielding an average value of $d\phi_w/dT$ of 7×10^{-5} ev deg.⁻¹ in the range 300–1100°K while Nottingham⁹ and D. B. Langmuir¹⁰ estimate this temperature coefficient at -4×10^{-5} . Assuming $d\phi_w/dT$ to be independent of temperature, Reimann's data give 4.54 ev for ϕ_W at 90°K while the Nottingham-Langmuir data yield the value 4.70 ev at this temperature. If, now, our value for the contact difference of potential W-Ba is combined with these two divergent values for ϕ_W one obtains 2.41 and 2.57 ev, respectively, for ϕ_{Ba} at 90°K. Taking into account a temperature coefficient for barium¹¹ of 5×10^{-5} the calculated values of ϕ_{Ba} at room temperature become 2.42 and 2.58 ev. But if, pending settle. ment of its sign and magnitude, the temperature coefficient of tungsten is put equal to zero the above computation, with Reimann's work function for tungsten and our Volta potential for W-Ba, gives 2.52 ev for the work function of barium at room temperature. The extent of the discrepancy between our value for ϕ_{Ba} and that of Jamison and Cashman is evidently contingent upon uncertain data for tungsten and we have, therefore, adopted 2.52 ev as the most probable value of the barium work function at room temperature. A possible structural dependence of this work function has not been considered. Such variations are almost certainly small for barium films deposited on glass at room temperature but may be significant when such films are compared with surfaces formed at liquid-air temperature.

Mention should, finally, be made of the high value, 2.70 ev, found for ϕ_{Ba} in the photoelectric work of Suhrmann and Deponte¹² who measured a single thick film prepared by direct vaporization of a raw barium sample. It has been our

experience that the first fusion of such a sample is invariably accompanied by a copious evolution of gas which, reabsorbed by the condensing surface, lowers rather than raises the work function.

The Work Function of Magnesium

In the preceding discussion of results for the Volta potential Ba-Mg emphasis has been placed upon the question of their consistency with the photoelectric data. The measurements obviously supply, also, an independent determination of the external work function of magnesium, with the barium, work function 2.52 ev, taken as the reference metal.⁵ The unweighted mean of the Volta potential values assigns 3.67 ev to ϕ_{Mg} in close agreement with the photoelectric value of Mann and DuBridge. Since, however, all of the contaminations likely to be present under the conditions of the experiment would be expected to lower the work function, it is probable that the value 3.78 ev corresponding to the maximum observed Volta potential deserves the greatest weight. Such a conclusion does not take into account a possible variation of work function with the crystal structure of the surfaces, and the observation that the maximum Volta potential was associated in at least one instance with a macroscopically crystalline rather than mirrorlike surface. As compared to barium, magnesium has a relatively rigid lattice and would be expected to be less capable of spontaneously establishing its equilibrium structure. A thick film of magnesium deposited on a soft barium surface and with equilibrium crystal faces sufficiently developed to show diffuse optical reflection represents a structure very different from that of a mirror film on glass and a different work function is to be expected. This structural effect, if real, bears out the tentative conclusion⁵ that the work function of a metal surface composed of equilibrium crystal faces is higher than that of a microcrystalline ("amorphous") film of the metal.

⁸ Reimann, Proc. Roy. Soc. A163, 499 (1937).
⁹ Nottingham, Phys. Rev. 49, 78 (1936).
¹⁰ D. B. Langmuir, Phys. Rev. 49, 428 (1936).
¹¹ Cashman, Phys. Rev. 52, 512 (1937).

¹² Suhrmann and Deponte, Zeits. f. Physik **86**, 628 (1933).