

incompatible with the symmetry character of a pure 3S state. The second cannot be discarded on an experimental basis but it ceases to be plausible if one admits the possibility, that ultimately the same causes may underly both the magnetic properties and the mutual binding forces of the proton and the neutron.

It is conceivable that the departure from any one of the two assumptions (*a*) and (*b*) would separately cause a considerable deviation from (20) but that for unknown reasons both together cancel each other very closely. Until reliable estimates of these deviations can be obtained we consider it, however, more likely that neither of them amounts to more than a few percents.

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The Contact Difference of Potential Between Barium and Zinc

The External Work Function of Zinc

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The methods of contact potential measurement described in previous reports of this series have been extended to zinc, for which the published work function data are discordant. Measurement was by the retarding potential method with variable anode, in tubes sealed from the pumps and gettered with vaporized barium. Barium was the reference metal and the measured surfaces of both barium and zinc were prepared by fractional distillation followed by revaporization of the middle fractions. In observations on three tubes and fifteen pairs of Ba-Zn surfaces the observed contact P.D., mean value 1.76 v, was reproducible and constant to ± 0.02 v. Combination of this value with the work function of barium, now well established at 2.52 ev, assigns the value 4.28 ± 0.02 ev to the work function of zinc at room temperature. The initial

measurement on a surface was taken within 8 seconds of its deposition. As a consequence of this small time lapse it becomes possible to answer the fundamental but neglected question of whether a work function measured under optimum vacuum conditions is characteristic of the clean metal or of a gas-contaminated surface in equilibrium with the residual gas. The rate of deposition of oxygen on zinc is estimated from the behavior of a tungsten "test surface" in a comparable vacuum. Since the regimes of measurement and of equilibrium gas film formation overlap and no change of work function with aging is detectable, it is concluded that the observed work function is characteristic of clean zinc. From the point of view of the adsorption processes involved, the measurements show that the mean time of sojourn of oxygen is much less on zinc than on tungsten.

THIS paper reports further results in a program of study of the external work functions of the pure metals as determined by measurement of their contact differences of potential with respect to a suitable reference metal, barium. Previous work under this program¹ has shown, (1) that the work functions of barium surfaces are reproducible to at least

± 0.01 ev when the surfaces are formed by fractional distillation in a sealed-off tube, and (2) that measurements of work functions by the contact potential method are now capable of the precision and accuracy characteristic of the best photoelectric work. Since the contact potential method, unlike the thermionic, is applicable to all the metals and, unlike the photoelectric, yields measurements of uniformly high sensitivity, it appears to offer the most promising

¹ P. A. Anderson, *Phys. Rev.* **47**, 958 (1935); **49**, 320 (1936); **54**, 753 (1938).

road to a systematic knowledge of the work-function characteristics of noncomposite metal surfaces.

For the purpose of testing our method of contact potential measurement, previous studies have been made upon metals for which the photoelectric data are especially reliable. The method is now being extended to metals for which the photoelectric data are contradictory, or for which no work function studies have yet been made under adequate experimental conditions. Zinc is one of the numerous common metals for which these data are discordant. Published values² range from 3.08 to 4.24 ev and the agreement has scarcely been improved by the most recent work. DeVoe,³ using the photoelectric method, has obtained 4.24 ev for the Fowler threshold while Oatley,⁴ employing a contact potential method, has reported a work function of 3.40 ev. Differences in the crystal structure of the zinc surfaces, determined by variations in the methods employed by different investigators for preparing their specimens, are no doubt partly responsible for the divergent values reported, but structural differences cannot account for work function deviations greater than a few decivolts. As has been pointed out in previous papers of this series, it is desirable that a standardized technique be selected for the preparation of each metal which is subjected to study, that the work function of this standard surface be determined under the most rigorous vacuum conditions, and that studies of the structural dependence of the work function be then referred to this standard surface. It has been suggested, also, that in work on most of the common metals, standard surfaces of reproducible structure can be best prepared by fractional distillation of the metal in a gettered vacuum, with deposition on a given substrate at given substrate temperature. This choice of technique, borne out by several extended series of measurements in this laboratory, has received further support from photoelectric measurements made at Northwestern by Cashman and his associates, who have developed a similar tech-

nique. Recent results on magnesium films prepared by this standardized method and measured in independent photoelectric and contact-potential studies have given work function values which agree to 0.01 ev.⁵ It was the purpose of the present work to extend this method to the

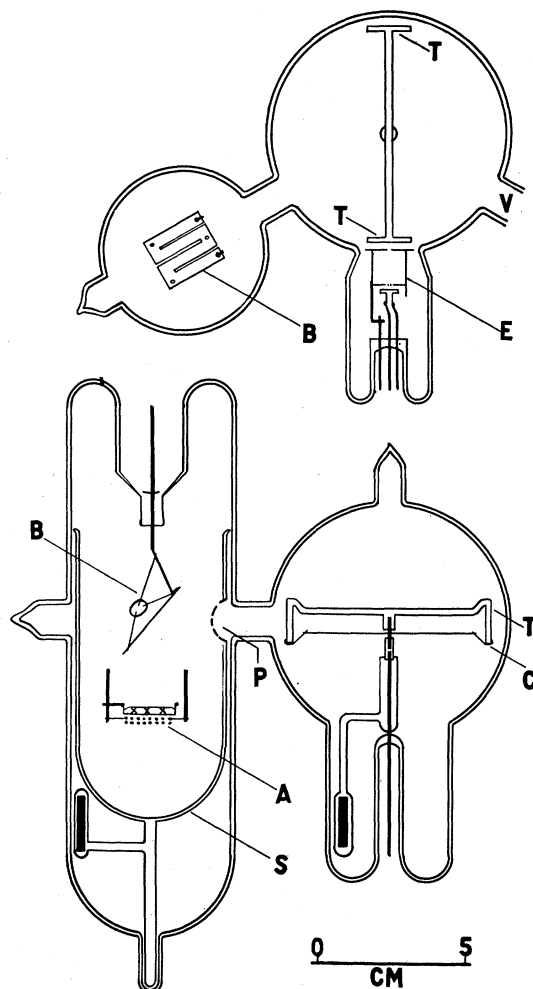


FIG. 1. The tube. First and second vaporizers, *A* and *B*, are mounted on single 3-lead press, one of 60-mil leads common. *A* (rotated 90° in sketch) comprises 20×20×5-mm pan of 1-mil Mo foil, with flat helical heater of 20-mil W wire. *B* is single 25×30-mm sheet of foil; Mo foil for barium, W foil for Zn (see text). Target assembly *TT* is of glass; rotatable on 60-mil W lead by magnetic traction on glass-enclosed armature. Contact *C* is 10-mil Pt wire embedded in face of target. Vapor shield *S*, with porthole *P*, is of glass with glass-enclosed armature. Electron gun *E* of 4-mil Ta foil; emitter 1-mil W foil 1.5 mm wide. A second vaporizing bulb, connected at *V*, is identical in design to the bulb shown.

² For a bibliography of the earlier work see A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (McGraw-Hill, 1932), p. 76.

³ C. F. DeVoe, *Phys. Rev.* **50**, 481 (1936).

⁴ C. W. Oatley, *Proc. Roy. Soc. A* **155**, 218 (1936).

⁵ R. J. Cashman, *Phys. Rev.* **54**, 971 (1938); P. A. Anderson, *Phys. Rev.* **54**, 753 (1938).

determination of the contact difference of potential between barium and zinc. Both metals were fractionally and multiply distilled and condensed on glass at room temperature.

EXPERIMENTAL PROCEDURE. TUBE DESIGN

The general features of the method and the electrical circuits have been described in previous reports. Details peculiar to the present measurements may be described in connection with the design of the tube, Fig. 1. The main improvement over our previous tubes lies in the construction of the first and second vaporizers and in their thorough shielding to eliminate any possibility of contamination of either metal by the other during the vaporizations. The first vaporizer *A*, providing for rapid fusion and controlled vaporization of a large charge (5–10 g) of metal by radiation heating, was an adaptation of a well-known method. The second vaporizer *B* is of new design which provides (1) a condensing surface of large area with consequent high efficiency in terms of the amount of metal finally utilized to that available in the middle fractions, and (2) very exact control of the rate at which vapor is delivered by the second vaporizer to the final condensing surface. This vaporizer was made by converting a 25×30-mm sheet of 1-mil tungsten or molybdenum foil into a grid by parallel cuts with a razor blade, as indicated at *B* in the plan sketch of Fig. 1. The grid was connected to its 60-mil tantalum current leads with tantalum rivets and held taut by a simple spider of 10-mil tungsten wires embedded in a Nonex bead and hooked through small holes in the grid, as indicated in the elevation sketch of Fig. 1. Heating current for the grid was supplied by a step-down transformer with continuously variable secondary voltage (Variac 80-A). The tubular shield *S*, mounted on a simple glass-to-glass thrust bearing as indicated, could be spun by a small permanent magnet and its porthole *P* brought into or out of register with the tube connecting vaporizing and measuring bulbs. During the preliminary fusions and vaporizations of barium and zinc both shields were kept closed; a shield was opened only for the deposition of a film on the target *T* and both shields were never opened simul-

taneously. In addition to their primary functions, the shields furnished an invaluable means of observing the progress of the vaporizations after the inner walls of the vaporizing bulbs had become coated with opaque layers of distilled metal. Slight rotation of a shield brought its porthole opposite an uncoated section of the outer bulb. Burning the heater of the first vaporizer at low current gave adequate illumination and approximate regulation of the rate of vaporization could be obtained by observation of the rate of deposition on the clear section of bulb thus exposed.

As in the tubes previously described, the measured films were laid down on a target which could be moved into position to receive any given fraction of either metal and then into the measuring position before the electron gun. The targets *TT* were, in this tube, duplicate Pyrex disks 18 mm in diameter, carefully mounted so that one reproduced the position of the other before the gun. A modification of the outgassing procedure applied in our previous work was necessitated by the relatively high volatility of zinc. The preliminary outgassing at 500–550°C was followed, after filling with dried air and introduction of the zinc and barium charges, by baking at 150°C rather than at 350°. Before sealing the tube from the pumps both barium and zinc were melted down two or three times to remove absorbed gases and these fusions were repeated after seal-off until approximately two-thirds of the original charges had been vaporized. The second vaporizers were flashed after each fusion to remove the condensates. The next fractions, amounting to an estimated 10–20 percent of the total charges, were utilized for the measurements and were distilled slowly to the second vaporizers. One of the targets was then coated with a thick mirror-like film of zinc by slow distillation from the second vaporizer and the potential setting for this surface determined. A succession of zinc films was then formed on top of the original zinc surface and each measured to determine the reproducibility and constancy of the potential setting for zinc. In certain experiments designed to test the possible effects of gas contamination, and discussed below, the films were deposited almost instantaneously by raising the voltage applied

to the second vaporizer. The zinc film was then brought before the second barium vaporizer and a succession of barium films laid down and measured. Thick films of zinc and barium were then formed alternately on this same target and the contact potential difference Ba-Zn thus checked repeatedly. The whole series of measurements was then repeated with the second target, starting with a thick film of barium in immediate contact with the glass target. This procedure was designed to show whether or not the work function of either metal was influenced by changing the substrate from glass to the other metal of the pair. No such influence was, however, detected.

MATERIALS

The barium employed in these measurements was taken from the same stock used in our earlier work and previously described. The zinc was the "spectroscopically pure" metal prepared by the New Jersey Zinc Company and kindly furnished to me by Mr. H. M. Cyr, with a spectroscopic analysis showing total impurities under 0.001 percent.

THE CONTACT DIFFERENCE OF POTENTIAL BETWEEN BARIUM AND ZINC

For all of the fifteen pairs of barium-zinc surfaces measured the contact differences of potential, mean value 1.76 v, were reproducible to less than ± 0.02 v. As indicated above, a measurement for a given "pair" of surfaces included in some instances the determination of potential settings for as many as five individual zinc surfaces and as many barium surfaces. Potential settings for the individual films of such a series were reproducible to ± 0.01 v for both zinc and barium and the observed contact P.D. between aging surfaces remained constant to within ± 0.02 v for periods of measurement extending from 8 seconds after deposition to several days. The measurements were the most satisfactory yet obtained for any pair of metals studied during the course of this program, in which barium has consistently shown a reproducibility limited only by the constancy of the measuring circuit but the second metal, e.g., silver, magnesium, has been less reproducible. The entire series of measurements on barium-

zinc included observations with three tubes, one of which was measured after the electrical circuits were rebuilt to improve their manipulation. Results for the three tubes were indistinguishable within the limits of reproducibility for any one tube.

THE EXTERNAL WORK FUNCTION OF ZINC

The work function of barium films prepared by the standard technique described above is now known with a high degree of probable accuracy to be 2.52 ev at room temperature. Combination of this value with our result of 1.76 ± 0.02 v for the contact difference of potential between barium and zinc assigns a value of 4.28 ± 0.02 ev to the external work function of zinc surfaces prepared by thermal vaporization and condensation on glass at room temperature. This result is to be compared with such of the earlier photoelectric and contact potential investigations of zinc as have been made under modern vacuum conditions. In Dillon's photoelectric study of polycrystalline and monocrystalline zinc⁶ the massive specimens were prepared in vacuum outside of the photoelectric tube, transferred quickly to the tube and subjected to prolonged pumping and irradiation with ultraviolet light. The irradiation produced progressive changes in the initial threshold and, finally, equilibrium values of 3.32 and 3.57 ev, respectively, for polycrystalline zinc and Zn (0001). Dillon tentatively attributed these values to gas-free surfaces but recognized the possibility that they might have been characteristic of gas-coated surfaces stable under the conditions of the experiment. In the later work of DeVoe,³ also done in Mendenhall's laboratory, the photoelectrically measured surfaces were prepared by distillation in the measuring tube itself under especially rigorous experimental conditions. The observed thresholds were highly reproducible and were constant over long periods of time. The Fowler threshold was found to be 4.24 ev at a residual pressure of 1.5×10^{-8} mm. This is the only published value in good agreement with the present results.

Since the present measurements were taken in sealed-off tubes it was not possible to test DeVoe's interesting observations: (1) that the

⁶ J. H. Dillon, Phys. Rev. **38**, 408 (1931).

work function of zinc remains unchanged as the residual air pressure is increased from 1.5×10^{-8} to 3×10^{-7} mm, but then drops rapidly to 3.5–3.6 eV as the pressure is increased to 10^{-6} mm, and (2) that the work function of zinc is insensitive to pure nitrogen up to at least 10^{-3} mm, the highest pressure tested. These observations are, however, borne out by the measurements of Oatley,⁴ who obtained a work function of 3.4 eV at a residual pressure of 10^{-6} mm. An extreme sensitivity of the work function to residual air pressure at pressures in the neighborhood of 10^{-6} mm, such as is indicated by DeVoe's curve, would account also for the work function fluctuations observed by Oatley.

EFFECTS OF GAS CONTAMINATION AT LOWEST RESIDUAL PRESSURES

Is the work function given by the present measurements, 4.28 eV, characteristic of clean zinc or must this value be attributed to a contaminated surface in equilibrium with residual gas? In work function determinations by both the photoelectric and contact potential methods it has been customary to utilize the most rigorous vacuum and outgassing techniques possible and then, provided only that the observed values are constant and reproducible, to assign these observed values to clean metal surfaces. But contaminating gas films must be built up to some degree even in the highest attainable vacuum and, after equilibrium between adsorbed film and bulk gas has been established, reproducibility and constancy of work function is to be expected for a contaminated as well as for a clean surface. The fundamental importance of this difficulty is generally recognized but the problem which it presents has received little explicit attention.

The experimental conditions which appear to be prerequisite to an attack upon the problem are: (1) the metal surface must be so prepared as to be initially free from gas, and (2) the first work function measurement must be made before a gas film, sufficiently concentrated to produce a measurable change in work function, has had time to build up. If these conditions are fulfilled and if further measurements show no drift in work function, we may conclude that the equi-

librium gas film is either too dilute to affect the work function or is composed of gases to which the work function is insensitive. While the first of these conditions can hardly be realized in its ideal form it is probably approached when the metal surface is prepared by multiple distillation in a gettered vacuum and the final vaporization is not too slow. If the maximum time lapse allowable under condition (2) could be calculated for any given metal-gas system it would then be possible to set up definite criteria for the measurement of any given metal. Such a calculation, involving time rates of formation of adsorbed gas films, evidently can be made only by a kinetic method of the Langmuir type and the minimum data required will not, in general, be available. In certain cases however, as shown below, enough information can be obtained from work function measurements themselves to enable us to get around this difficulty.

In the present measurements no drift in work function could be detected for freshly deposited zinc surfaces within a series of measurements beginning 8 seconds and extending to several days after formation of the surface. To obtain an estimate of the amount and probable effects of the gas deposited in the 8-second interval we compare the behavior of zinc with that of a suitably chosen "test surface" which is initially freed from gas and, like zinc, measured in a tube which has been gettered by vaporized barium, i.e., under a residual gas of comparable pressure and composition. The test surface is so selected that (1) it is sensitive to the same component of the residual gas as is zinc, and (2) its adsorption mechanism for this active gas is already known. The behavior of the test surface then furnishes an index to the rate at which the active gas, of otherwise unknown concentration, is supplied to the zinc surface. Since DeVoe's gas tests show that oxygen is the active contaminant for zinc, tungsten suggests itself as an ideal test surface. The reflection coefficient of tungsten for oxygen is known to be extremely small and the work function of tungsten is extraordinarily sensitive to traces of adsorbed oxygen. Now it has been found in numerous published⁷ and unpublished measurements in this laboratory that tungsten, cleaned by flashing to 2800°K

⁷ Reference 1; first citation.

and then allowed to cool, invariably shows a drift of work function, but that, in well gettered tubes, this drift does not become measurable until several minutes after flashing. In tubes immersed in liquid air the drift may be postponed for as much as 20 minutes. The drift is toward higher work function and continues for several hours before equilibrium is attained. In the earliest stages of adsorption n , the number of adsorbed molecules per unit surface of adsorber, is too small to affect the time rate of increase in n and we may write

$$dn = (1 - \alpha)\nu dt,$$

where α is the reflection coefficient and ν is the number of oxygen molecules which strike unit area in unit time. The effect of the inert components of the residual gas upon α presumably will be of the same order of magnitude for both tungsten and zinc and in the gettered vacuum ν will be approximately the same for both surfaces. In terms of this equation our observations on tungsten show that dn/dt is so small that n attains the extremely small value necessary for detection only after a time interval of the order of minutes. Turning to zinc we may conclude, then, that even if all the oxygen molecules which strike its surface in 8 seconds were to remain adsorbed their number would be insufficient to produce any significant change in work function within this time interval. From the absence of a time drift of the work function of zinc, and its

occurrence for tungsten, we may infer, furthermore, that the mean time of sojourn, τ , of an adsorbed oxygen molecule must be much smaller on zinc than on tungsten. For it follows from purely statistical considerations which are independent of adsorption mechanisms, that for any equilibrium film of adsorbed gas

$$\tau = n/\nu.$$

Even when ν is small, τ is so large for oxygen on tungsten that at equilibrium n approaches the total number of adsorbing positions available per unit area. The fact that zinc, although sensitive to oxygen, shows no drift at these small values of ν can be accounted for only if n and τ are so small that the equilibrium film when finally completed is too dilute to produce a measurable change in the work function. We have, then, reasonably convincing evidence that the work function of a zinc surface prepared and measured in a barium gettered vacuum is characteristic of the uncontaminated metal. It may be mentioned, finally, that from the point of view of residual gas effects the contact potential method possesses a unique advantage over emission methods for determining work functions. Since it measures the average work function of a surface, the contact potential is relatively insensitive to slight contaminations which, localized on emitting areas, may have a relatively serious effect upon the emission characteristics of the surface.