Photoelectric Properties of Barium and Calcium*

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With a photoelectric cell in which Ba was fractionated and repeatedly distilled, values of φ_0 at room temperature, as obtained by Fowler's method, were found to be 2.520 and 2.510 electron volts, the difference being attributed to either differences in crystal structure or chemical purity. For both conditions of the surface, the cell showed extraordinary constancy of work function. Measurements 100°C above room temperature yielded a temperature coefficient of $(2.2\pm0.7)\times10^{-5}$ ev/°K. The absolute photoelectric yield of the surface was determined. The optical reflection coefficient was found to vary from 43 percent at 4000A to 63 percent at 7000A. The work function of a Ca surface prepared by single distillation was 2.706 ev. After repeatedly heating the surface to 100°C the data did not fit Fowler's theoretical curve. The departures were consistent with the assumption that, after heating, the surface was not homogeneous. Analysis of the data gave evidence of two emitting surfaces having work functions differing by approximately 0.2 ev.

SEVERAL writers have pointed out that the work function of a metal should show a temperature dependence.[1] The existing evidence for a temperature coefficient is based either on considerations of the constant A in Richardson's equation, contact potential measurements, or photoelectric measurements over a relatively large temperature range. The experimental evidence which gives a direct measure of the temperature dependence is meager and not conclusive.[2] The use of a large temperature range is not desirable since the gas content of the tube may be increased when the surface is heated to relatively high temperatures; also large temperature changes may cause a change in crystal structure.

If a relatively small temperature range is used, changes in work function of the order of 0.001 ev must be measured; hence, a valid determination can be made only if a surface shows extreme stability. Assuming the validity of Fowler's method,[3] work function differences of this order of magnitude can be definitely established.

However, it has been found that not all photoelectric data can be fitted to Fowler's theoretical curve, even in the range near the threshold where the approximations involved in the theory are valid. An accurate fit is possible only when the surface is homogeneous. The production of such surfaces which are stable over a given temperature range has proved to be a difficult problem.

The present work was undertaken in an attempt to determine directly the temperature coefficients of the work function for the alkaline earth metals. The work is not complete at present; however, information has been obtained concerning the temperature coefficient for a Ba surface, the absolute photoelectric yield of a Ba surface, and emission from a nonhomogeneous Ca surface. It is felt that a report on this work might be of interest at the present time.

ACCURACY OF MEASUREMENTS

There are four quantities which must be measured in order to fit photoelectric data to Fowler's theoretical curve; namely, temperature, wave-length, photoelectric current, and radiation energy. Of these, the temperature measurement is by far the least critical. An error of even a few degrees at room temperature would cause a negligible error in the work function, since the horizontal shift depends upon $1/T$ and the computation of the work function from the shift depends upon T. A large error in temperature measurement, however, would result in a poor fit to Fowler's theoretical curve.

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[1] P. W. Bridgman, Phys. Rev. **31**, 90 (1928); K. F. Herzfeld, Phys. Rev. **35**, 248 (1930); J. A. Becker and W. H. Brattain, Phys. Rev. **45**, 694 (1934); L. A. DuBridge, *Actualités Scientifiques et Industrielles*, No. 268, Paris, 1935; W. B. Nottingham, Phys. Rev. **49**, 646A, 649A (1936); E. Wigner, Phys. Rev. **49**, 696 (1936).

[2] Cf. Becker and Brattain, and DuBridge, reference 1; also R. Suhrmann and A. Schallamach, Zeits. f. Physik **91**, 775 (1934); W. B. Nottingham, Phys. Rev. **49**, 78 (1936); D. B. Langmuir, Phys. Rev. **49**, 428 (1936).

[3] R. H. Fowler, Phys. Rev. **38**, 45 (1931); E. Rudberg, Phys. Rev. **48**, 811 (1935).

Before the wave-length measurements are discussed attention should be called to the fact that the radiation used must be free from scattered light; also, if a source of continuous spectrum is used the dispersion should be adequate. Since line sources are subject to fluctuations, a continuous source is desirable for work in the visible range. Two single prism instruments were found entirely unsatisfactory due to scattered light; in the work here reported a double Van Cittert glass monochromator was used. Direct wave-length measurements of the resolved light were made with a Hilger spectrometer. The wave-length spread for the slit width used was approximately 8 angstrom units at 4000A and increased to about 37 units at 5000A. The effect of this finite range of wave-lengths was analyzed and it was found that the use of the mean wave-length introduced a negligible error in the determinations of work functions to 0.001 ev. The accurate determination of small changes in work function is not affected by this approximation.

Current measurements were made using an FP–54 Pliotron tube and the circuit of DuBridge and Brown,[4] all measurements being made in a shielded room. For each setting of the monochromator a series of deflections was taken, the probable error for all except the two smallest deflections being less than one percent for the room temperature data and less than two percent for the high temperature data.

An improved form of Nichol's radiometer[5] was used to obtain the energy calibration. The interception of light by the radiometer vane was checked by a microscope mounted behind the vane. The amount of light not striking the vane was small and very nearly a constant fraction of the total. This was established by simultaneously measuring radiometer deflections and the photo-current of a cell illuminated by light that failed to strike the vane. The accuracy of the energy measurements was estimated at better than one percent. The radiometer was calibrated for absolute energy by comparison with a lamp checked at the Bureau of Standards.

The quantities thus far discussed relate to the

[4] L. A. DuBridge and H. Brown, Rev. Sci. Inst. 4, 532 (1933).
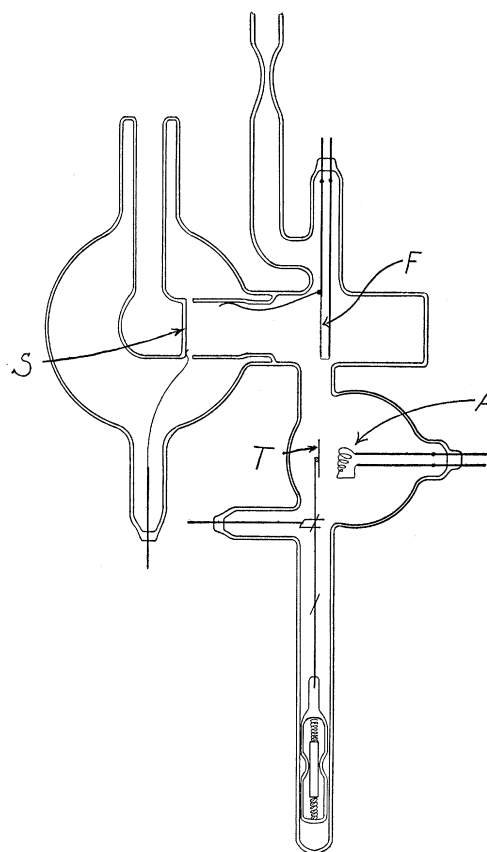[5] B. J. Spence, J. Opt. Soc. Am. 6, 625 (1922).

FIG. 1. Photoelectric cell used in work on Ba.

accuracy of plotted points. The determination of the work function (or temperature coefficient of the work function) depends upon the horizontal shift necessary to superimpose the experimental data upon Fowler's theoretical curve. In order that the accuracy of the curve fitting be consistent with the accuracy of the experimental data it was necessary to obtain data over a sufficiently wide frequency range, and to plot to a large scale. The plots such as Fig. 3 were approximately 40×50 cm. The frequency range used corresponded to approximately 0.6 ev.

EXPERIMENTAL PHOTO-CELLS; OUTGASSING

Barium

The construction of the cell used in the work on barium is shown in Fig. 1. The great efficiency of Ba as a "getter" metal might at first seem disadvantageous if "clean" Ba surfaces are to be investigated. That this characteristic permits
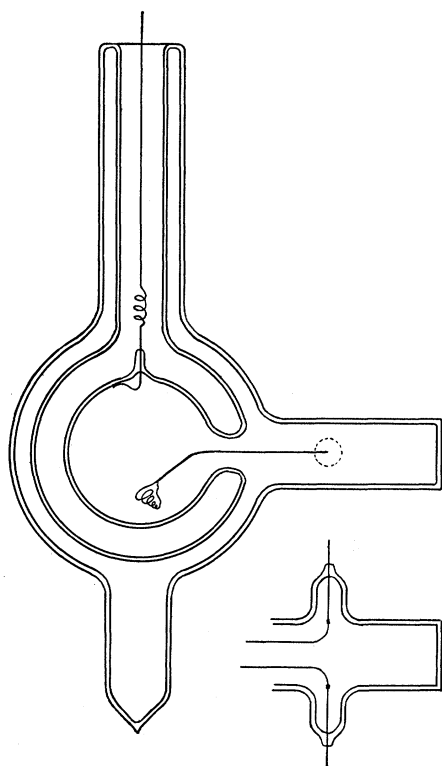
FIG. 2. Photoelectric cell used in work on Ca.

the design of a cell which possesses distinct advantages will be evident from what follows. Before the introduction of the Ba, the tube was

baked at temperatures up to 550°C for about one week and the metal parts were accorded a severe heat treatment. Dry nitrogen was then admitted to the system and a freshly turned slug of Ba was placed in the spiral filament A. A week of pumping and baking followed at a lower temperature (350°C) during which time all metal parts were frequently heated as before. The Ba was progressively heated to higher and higher temperatures until it finally melted and formed a large drop around the lower turns of the filament. After a considerable quantity of Ba had condensed on the lower bulb wall the tube was sealed off. The work function of this surface was approximately 0.15 ev lower than that finally obtained, due no doubt to the clean-up of gas released in the sealing-off process.[6] More Ba was vaporized until approximately one-third had condensed on the lower bulb wall.

A magnetic control served to bring the tantalum plate, T, down to the lower chamber where it received a coating of Ba. After being raised and turned the plate was heated by radiation from the filament, F, so the resulting vaporization formed a deposit on the plate, S. Several deposits were made in this way until an opaque coating was formed. The deposit of Ba on the

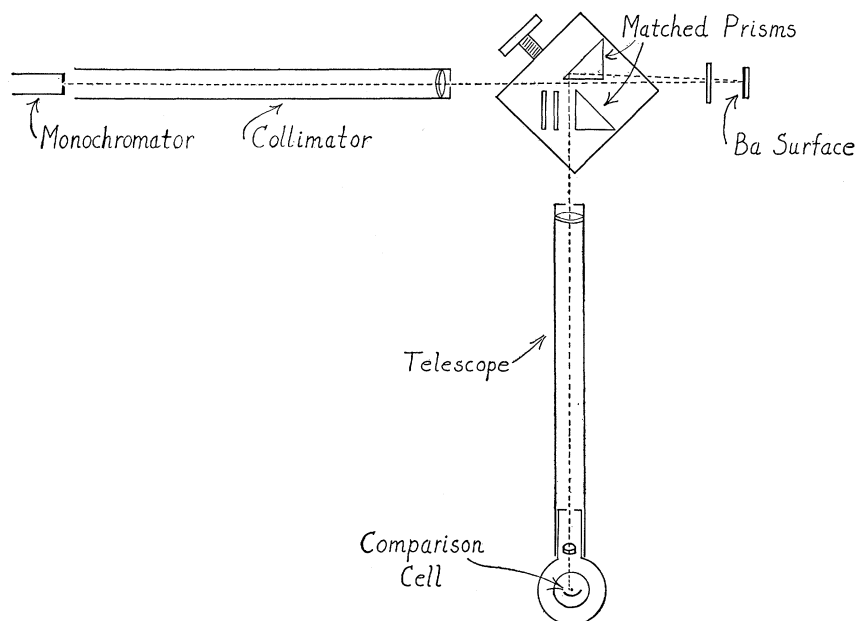[6] R. J. Cashman and W. S. Huxford, Phys. Rev. **48**, 734 (1935).

FIG. 3. Apparatus used for the measurement of optical reflection.

walls of the horizontal tube served as anode, contact being made by a wire supported by the filament leads.

Such a method of fractional distillation plus repeated distillation should yield effectively gas free layers of higher chemical purity. Since the work function did not change measurably with time after deposit, the vacuum conditions were considered adequate.[6]

Calcium

The work done with Ca has been confined so far to a cell using a single distillation. The type of cell used is shown in Fig. 2. The outgassing procedure was essentially the same as that just

TABLE I. *Reflection coefficient of barium.*

Wave-length in angstroms	4000	4500	5000	5500	6000	6500	7000
Reflection Coefficient (%)	43.	45.	48.	52.	55.	59.	63.

TABLE II. *Data from which the Fowler plots of Fig. 5 and Fig. 6 were made. Wa was computed on the basis of two free electrons per atom.*

	Current/unit intensity	
$\lambda(A)$	$T = 295.4°K$	$T = 397.2°K$
4189	124	111
4248	101	91.9
4310	81.1	74.5
4379	62.2	56.8
4452	46.6	42.5
4524	33.0	30.0
4572	25.7	24.0
4614	19.7	18.8
4641	16.7	15.9
4666	13.4	13.1
4698	10.9	10.7
4726	8.42	8.46
4756	6.55	6.60
4776	5.28	5.61
4808	3.63	4.06
4841	2.45	2.78
4874	1.44	1.95
4908	.88	1.36
4942	.52	.83
4976		.55

TABLE III. *Values of the work function for a barium surface as obtained from five room temperature and three high temperature determinations.*

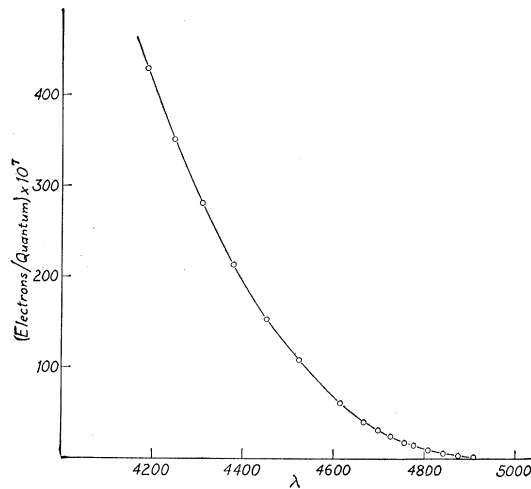| $T = 295.4°K$ Horizontal Shift	$T = 397.2°K$ Horizontal Shift
98.64	73.43
98.69	73.48
98.72	73.44
98.67	
98.69	Mean 73.45
Mean 98.68	(Mean) $\varphi_0 = 2.5128$ ev.
(Mean) $\varphi_0 = 2.5106$ ev.	

FIG. 4. The absolute photoelectric yield of a Ba surface as a function of wave-length.

described. A single distillation cell, however, is not suited to the determination of the temperature coefficient, particularly for elevated temperature measurements, since residual gas trapped in the first condensed layers very likely diffuses to the surface. Also unless the optical reflection coefficient varies but little over the frequency range used, a multiple reflection cell may not be desirable.

OPTICAL REFLECTION COEFFICIENT APPARATUS

In order to discover any possible correlation between photoelectric and optical properties. the reflectivity was measured as a function of wave-length and temperature using a photometer arrangement shown in Fig. 3. This device permits alternate readings of incident and reflected light to be made by a simple translation of matched prisms, with the assurance that the two beams will strike the same spot on the comparison cell. Since many commercial photo-cells respond differently over their surfaces such a method seems necessary. Measurements were limited to the range over which the lenses were achromatic; the window and reflecting surface must be approximately plane.

RESULTS

Optical reflectivity of barium

Table I shows the results of the reflection coefficient determinations. No correlation be-
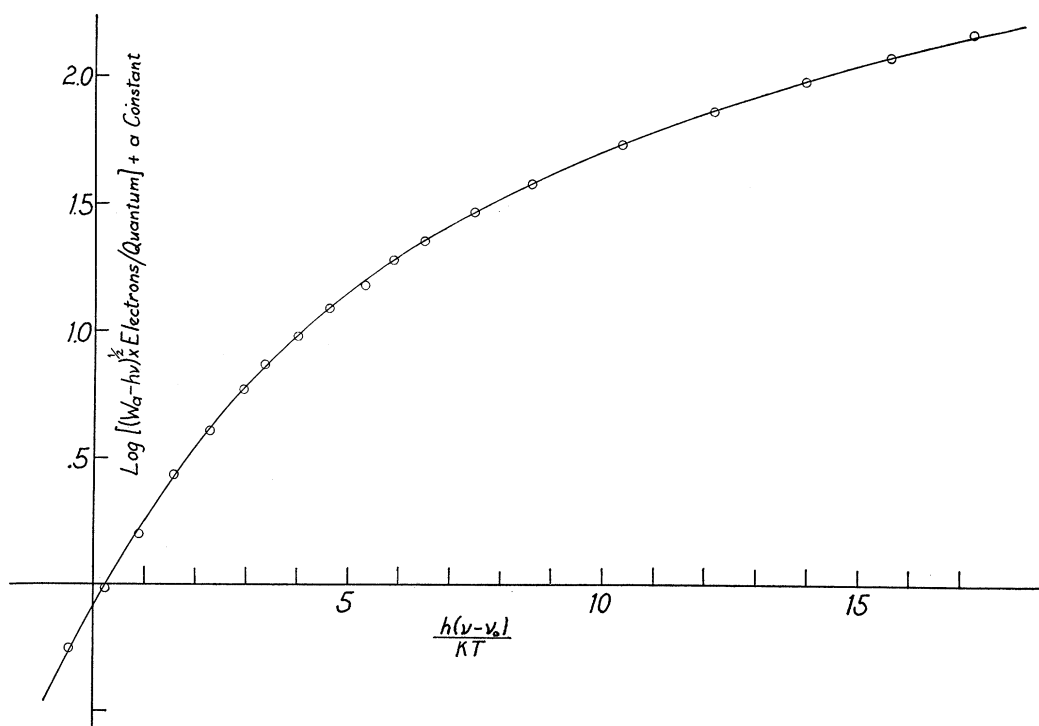
FIG. 5. Typical Fowler plot for a Ba surface at 295.4°K. Horizontal shift 98.65; $\varphi_0 = 2.510$ ev.

tween photoelectric emission and reflection coefficient was observed; also the value of reflection coefficient at dry ice temperature was no different than at room temperature, as the theory of Kronig[7] predicts. The values are considerably higher than those obtained by O'Bryan[8] using a polarized light method.

Room temperature work function of Ba

By using Fowler's method, the work function obtained for the initial series of deposits was 2.520 ev[9] as found from measurements made from two hours to three months after laying down deposits. During this period the surface experienced no large temperature changes with the exception of being lowered to $-77°$C. The variation of photoelectric efficiency of this

surface as a function of wave-length is shown in Fig. 4. The low efficiency obtained is characteristic of gas free metals.

No change in the room temperature work function was found after lowering the temperature of the surface to $-77°$C. Lowering the temperature of the surface to liquid-air temperature so changed the surface that subsequent room temperature data failed to fit Fowler's curve accurately. The experimental curve gave evidence of a nonhomogeneous surface (an analysis of photoemission from such surfaces will be given later using data obtained with calcium). A tentative explanation of this failure to fit Fowler's curve is based on the hypothesis that the extremely low temperature produced such stresses between the barium layer and the glass base that the surface was permanently strained. Such a condition might presumably disturb the original microcrystalline character of the surface and thus produce areas having different emission characteristics.

A new deposit of barium failed to give data in good accord with theory, but a series of heat treatments totaling about 6 hours at 120°C

[7] Kronig, Proc. Roy. Soc. **A124**, 409 (1929); **A133**, 255 (1931); Mott and Zener, Proc. Camb. Phil. Soc. **30**, Part 2 (1934).

[8] H. M. O'Bryan, J. Opt. Soc. Am. **26**, 122 (1936).

[9] Work function values given here will be found to differ slightly from those given by us in previous reports. Those given here were obtained by plotting electrons $\times (Wa - h\nu)^{\frac{1}{2}}/$ quantum as ordinate, while those previously reported were obtained from current/unit intensity plots. For a discussion of different methods of plotting see, R. J. Cashman and N. C. Jamison, Phys. Rev. **50**, 568 (1936).
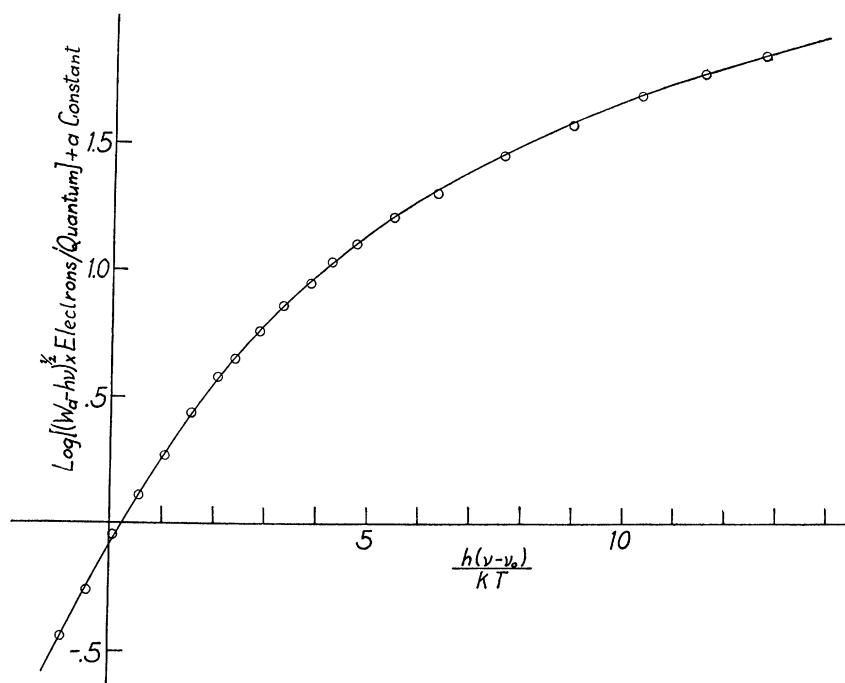
FIG. 6. Typical Fowler plot for a Ba surface at 397.2°K. Horizontal shift 73.43; $\varphi_0 = 2.512$ ev.

brought about a surface condition furnishing data in excellent agreement. A typical room temperature Fowler plot is shown in Fig. 5 with the data given in Table II. The results of five room temperature determinations are shown in Table III, the mean value being 2.5106 ev. We do not maintain that these work functions are accurate to 0.0001 ev; the fifth significant figure has been retained only for purposes of comparison with values obtained at a higher temperature. Between these runs the surface was heated to temperatures of 100° to 140°C for a total time of about 150 hours, indicating the existence of an extremely stable surface over this temperature range.

It will be observed that there is a difference of 0.01 ev between this mean value and that obtained for the initial series of deposits. We do not believe that the change is due to gas contamination, but rather that it is to be attributed either to a change in crystal structure or to a change in chemical purity.

These values of the work function of Ba are higher than any previously reported. Early determinations of the work functions of the alkaline earths were generally too low due to

gas contamination.[6] It is of interest to compare our results with those of Anderson[10] who obtained 2.39 ev for Ba using contact difference in potential measurements with reference to tungsten. These measurements were carried out on surfaces prepared by fractional distillation in a gettered vacuum. The discrepancy can hardly be explained on the basis of gas contamination; the possibility of a slight difference in chemical purity exists. There might also be an effect on the crystal structure due to the influence of the backing materials and the temperature at which the deposits were made. A tentative explanation which seems reasonable is based on the work function of tungsten, 4.52 ev, used by Anderson. This value is the heat function and has not been corrected for a possible temperature dependence (Anderson's measurements were made at liquid-air temperature).

Temperature coefficient of the work function

The horizontal shifts and the mean value of the work function for 397.2°K are given in Table III. A typical set of data at this tempera-

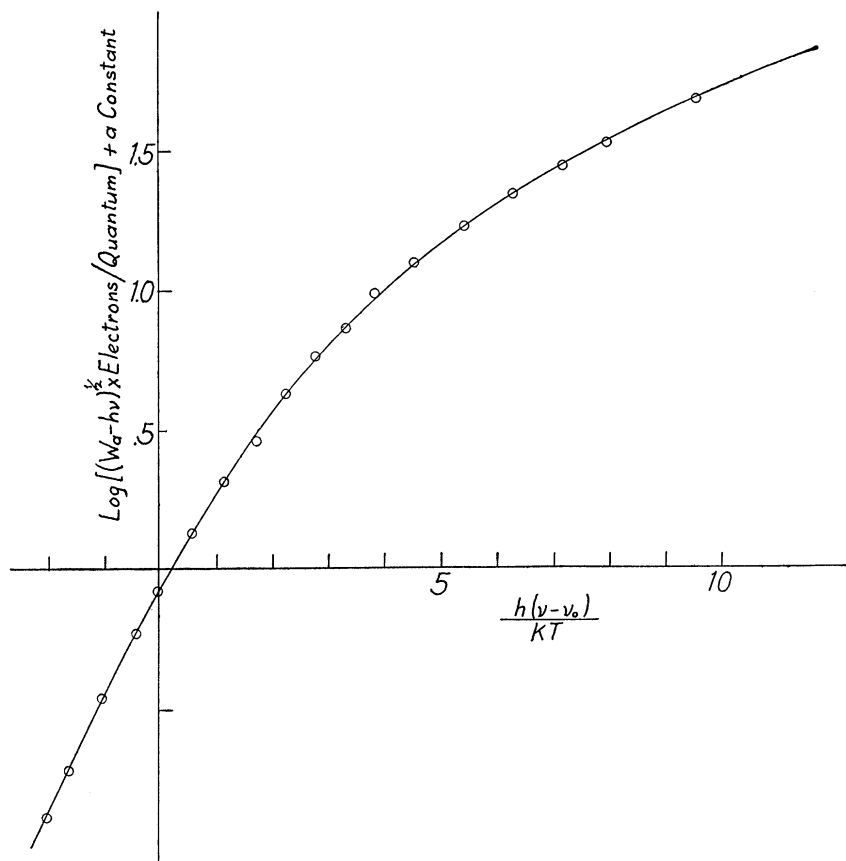[10] P. A. Anderson, Phys. Rev. **47**, 958 (1935); **49**, 320 (1936).

FIG. 7. Typical Fowler plot for a Ca surface at 298.4°K. Horizontal shift 105.28; $\varphi_0 = 2.706$ ev.

ture is shown in Fig. 6, the numerical data being given in Table II. A comparison of these values with the room temperature values shows a positive temperature coefficient of $(2.2\pm0.7)\times10^{-5}$ ev/°K. It appears that this change in work function is due explicitly to temperature and not to other causes. It is well known that surfaces which are slightly contaminated with gas are erratic in their behavior. As will be cited in the discussion of the work on Ca, minute amounts of gas may be expected to give data not in agreement with Fowler's theory, and in this case also the surfaces do not exhibit the stability shown by the Ba specimens.

We do not maintain that the value given is more than an estimate for the particular surface studied for the given temperature range. The temperature coefficient would be expected to depend upon the crystal state of the surface and may well be a function of temperature. The

influence of the backing material on the expansion of the metallic layers may be important.

Data taken at dry ice temperature were not so accurate as those taken at higher temperature; however an estimation of the work function at the low temperature showed it to be slightly lower than the room temperature value.

Data obtained at 224°C failed to fit Fowler's curve accurately as did also subsequent room temperature data. A situation had apparently arisen similar to that which occurred when liquid-air temperature measurements were attempted.

Value of A in Richardson's equation

If one assumes that the departure of the value of A from the theoretical value of 120 amp./cm^2 °K^2 is due entirely to a temperature coefficient of the work function, that is, that the transmission coefficient for electrons is unity and that

field effects and surface irregularities are negligible, one can compute the value of A for a Ba surface emitting thermionically.[11] Assuming a constant temperature coefficient of 2.2×10^{-5} ev/°K, A becomes approximately 93 amp./cm² °K². It is well known that most metals have an experimental value of A less than 120; this is also predicted by the theory of Wigner.[1]

PHOTOELECTRIC PROPERTIES OF CA AND PHOTO-EMISSION FROM NONHOMOGENEOUS SURFACES

With a single distillation cell the mean value of the work function for a Ca surface, as determined by Fowler's method, was 2.706 ev with the greatest deviation from the mean for seven determinations being 0.004 ev. A typical plot is shown in Fig. 7. The work on calcium was preliminary to that on Ba and the measurements were not as accurate. After repeatedly heating the surface to 100°C the results obtained were somewhat erratic; surface conditions obviously had been altered (in this case very likely due to gas) and the data did not in general fit Fowler's curve accurately. The departures from the curve were consistent with the assumption that, after heating, the surface was not homogeneous. Such a set of data is shown in Fig. 8. That this distribution of points can be fitted to a theoretical curve is demonstrated by the close fit to the full line curve which represents the computed emission from two surfaces, according to Fowler's theory, one surface having a work function of 2.728 ev and the second with $\varphi_0 = 2.537$ ev, the first surface having a greater effective area by a factor of 69. The term "effective area" is used to include such factors as optical absorption, electron reflection, emission efficiency, etc. The two dashed curves are Fowler plots for the two surfaces whose existence is assumed.

In the discussion of the work on Ba it was stated that some plots suggested the existence of a nonhomogeneous surface. These plots showed small departures from Fowler's theoretical curve. The departures were not great enough, however, to warrant the analysis of the curves as done for the nonhomogeneous Ca surface discussed above.

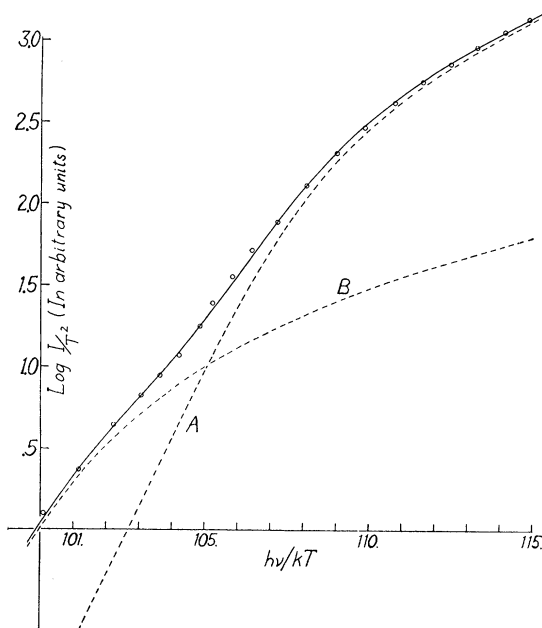[11] J. A. Becker, Rev. Mod. Phys. 7, 95 (1935).

FIG. 8. The full line curve represents the computed emission from two surfaces according to Fowler's theory. The Fowler plots for the two surfaces assumed are shown by the dotted line curves. For curve A, $\varphi_0 = 2.728$; for curve B, $\varphi_0 = 2.537$.

The suggested nonhomogeneous character of the Ba surfaces was attributed to areas showing slightly different crystal structure or orientation.

In view of the experimental evidence that patches do exist in the case of thorium on tungsten,[11] the above explanation of the data seems reasonable. The design of the tube was not suited to the investigation of possible field effects.

Fig. 8 not only serves to demonstrate the possibility of investigation of nonhomogeneous surfaces but also emphasizes the value of taking data over a sufficiently wide range. Had experimental points been taken over but a short range of wave-lengths, a fair fit to Fowler's theoretical curve might have been obtained and a false value of work function determined. An accurate fit to Fowler's curve over the long wave-length range denies the existence of a second surface having a slightly lower work function; also an accurate fit to Fowler's curve over the short wave-length range denies the presence of a second surface having a slightly higher work function.