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April 1968

DETERMINATION OF THE WORK FUNCTIONS OF
SELECTED METALS AND INORGANIC COMPOUNDS

Prepared by
Denver Research Institute
University of Denver
Denver, Colorado

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Prepared by
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Sandia Laboratories

under

Contract No. 57-1061

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SUMMARY

Equipment was purchased and assembled for the determination of photoelectric work functions by the Fowler and Anderson techniques. The work functions of titanium, erbium, vanadium, and chromium were determined both thermionically and photoelectrically. The work functions of the titanium-hydrogen and the erbium-hydrogen systems were determined photoelectrically as a function of hydrogen composition. In the photoelectric work the metals were evaporated onto a nickel substrate under very high vacuum conditions. The work function of the nickel substrate was determined before the other metals were evaporated.

The results obtained were as follows:

Nickel: Photoelectric work function values of 4.30, 4.54, 4.52, 4.80 and 4.50 eV.

Titanium: Thermionic, Richardson work function of 3.77 eV. Photoelectric work functions of sheet titanium from 3.97 to 4.10 eV. Photoelectric values of 3.52 and 3.60 eV for evaporated titanium.

Erbium: Thermionic, Richardson work functions of 3.10 ± 0.04 and 3.11 ± 0.09 eV (Note: wires believed to be contaminated with oxide). Photoelectric work functions of 3.10 and 2.75 eV.

Vanadium: Thermionic work function of 4.66 ± 0.05 eV. Photoelectric work function of 4.07 ± 0.05 eV.

Chromium: Thermionic work function value of 4.42 ± 0.07 eV. Photoelectric work functions of 4.83 and 4.55 eV.

Titanium-hydrogen system: Photoelectric work function decreased to 3.30 eV before the composition reached $\text{TiH}_{0.05}$ and remained at this value with increasing hydrogen content.

Erbium-hydrogen system: Hydrogen did not change the work function of the metal. An increase in work function was observed at high hydrogen contents but this may have been due to loss of hydride film from the substrate.

The limits of error for the photoelectric work function values where not given above do not exceed ± 0.1 eV based on visual observation of graphical data.

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I. INTRODUCTION

This is the final report of a research program entitled "Determination of the Work Functions of Selected Metals and Inorganic Compounds" carried out under contract (Contract Numbers 11-8120 and 57-1061) between the Sandia Corporation and the Metallurgy Division of the Denver Research Institute, University of Denver. The purpose of this program was to determine the work functions of the metals: titanium, erbium, vanadium, and chromium; where possible to determine the effects on the work function of contaminants on the surfaces of these metals; and further to determine the work function of the titanium-hydrogen and erbium-hydrogen systems as a function of hydrogen composition. The work functions of the metals were determined both thermionically and from photoelectric emission. The work functions of the metal-hydrogen systems were determined at room temperature from photoelectric emission.

This report will describe the equipment purchased and assembled for determining work functions from photoelectric emission data; the method of treating these data to obtain work functions; and the results obtained for the metals and metal-hydrogen systems. The thermionic work on the four metals was completed in the summer of 1966 and is described extensively in a Summary Report (DRI #2344) submitted in August of 1966. A complete description of this work will not be repeated here. However, the results of the thermionic work will be compared to the results obtained from photoelectric measurements.

II. EQUIPMENT AND PROCEDURES FOR PHOTOELECTRIC EMISSION MEASUREMENTS

In the photoelectric effect, electrons are ejected from a surface under the influence of light. In order to measure the photocurrent, the emitter and collector must be contained in a high-vacuum system, a light source must be directed at the emitter, provision must be made for applying a potential difference between emitter and collector, and a sensitive instrument must be used for measuring the current. In the Fowler method of determining work functions from photocurrent measurements (to be described in detail in a following section), the photoelectric yield (electrons emitted per incident photon) must be determined as a function of the frequency of the incident light. This means that in addition to the items mentioned above, one must provide a monochromator to distinguish the frequency of the incident light beam, and an instrument to measure the absolute intensity of the light beam in order to determine the number of incident photons. For experiments carried out on metal-hydrogen systems an auxiliary gas-handling system (Sieverts' apparatus) must be provided for adding known amounts of gas to be absorbed by the metal. An apparatus was designed and constructed incorporating all of the features just mentioned. A schematic drawing of this apparatus is shown in Figure I.

A. Diode

In the upper center of Figure I is shown the diode or phototube. This is a demountable tube about one foot in height. The tube itself is of Pyrex, two and one half inches in diameter with glass-to-metal seals at the end plates. Not shown in the figure is an arm half way up the tube extending towards the monochromator. At the end of this arm is an optically flat quartz window one and one half inches in diameter. Varian flanges were used for the end plates. The upper end plate was modified by Ceramaseal to contain eight insulated electrical feed throughs. The lower end plate was modified, again by Ceramaseal, to provide four radially directed feed throughs. The electrodes inside the diode were made of high purity nickel. Provision is made for attaching a one inch square metal piece to the emitter electrode directly in front of the quartz window. In all but the very first experiments in which a piece of titanium sheet was used as the emitter, the material to be studied was evaporated in situ under high-vacuum conditions onto a nickel substrate. The evaporator consisted of a strand of three-ply tungsten wire bent in the form of an open circle (so as not to impede the light beam) and situated directly in front of the one inch square nickel substrate. The

Figure I. Schematic of Experimental Setup For Work Function Measurements

material to be evaporated, in the form of small diameter wire, was wrapped around the tungsten evaporator. The evaporator was resistance heated. To avoid overheating the glass walls of the diode and the glass to metal seals, evaporations were carried out in a stepwise manner, thus depositing a series of thin films on the nickel substrate and the diode walls. The quartz window was protected by an iron disc (manipulated with a magnet) during evaporation.

B. High Vacuum Components

The high-vacuum components shown below the diode in Figure I consist of a Varian vac sorb pump, a Varian 50 liter per second vacuum pump and power supply, and a Varian nude ionization gauge and power supply. After bake out of the diode at about 350°C and of the tubulation and valves at about 150°C, a pressure in the 10^{-9} mm of Hg range was consistently achieved.

C. Photocurrent Measurement

Photocurrents were measured using a Cary vibrating reed electrometer, Model 31. It was found necessary to shield the diode completely in heavy-gauge metal and to mount the preamplifier of the electrometer directly above the shield in order to eliminate background noise. With these arrangements the instrument worked very satisfactorily. The photocurrents measured were of the order of 10^{-13} to 10^{-9} amperes.

A Keithley regulated power supply, Model 240, which is capable of supplying direct current voltages of from 0 to 1000 volts with an accuracy of within 1%, was used to apply a potential difference between emitter and collector. It was found that 100 volts was more than sufficient to insure saturation of the photocurrent (all emitted electrons collected), and this potential was commonly used in the experiments.

D. Optical System.

The optical system consists of a Bausch and Lomb, Model 33-86-48, 500 millimeter grating monochromator with achromatic condenser lens, a 100 watt mercury-arc source (Hanovia, Model 43164), a calibrated Epply thermopile with quartz window, and a Keithley, Model 148, micro-voltmeter. In practice the light from the mercury arc passes through the monochromator and the monochromatic light from one of the emission lines of the arc is focused on the surface of the emitter. In most

experiments the monochrometer's exit slit width was 1 mm. The slit height is adjusted so that the slit image falls completely on the surface of the emitter. In most experiments the area of the slit image was 0.95 cm^2 . After making a photocurrent measurement a mirror is interposed in the light beam directing the light to the thermopile. The thermopile is situated the same distance from the exit slit of the monochrometer as is the emitter. Thus the slit image size is the same on the aperture of the thermopile as it is on the emitter. The output of the thermopile is measured by the microvoltmeter, and the reading is converted to energy by the calibration factor 0.055 microvolts per microwatt/ cm^2 . Since the thermopile was calibrated with the aperture filled with light, it is necessary to have this condition obtain during the experiments. This is the main reason for using an exit slit width of 1 mm.

Determining the intensity of the light in the manner described above proved to be the most difficult part of the experimental procedure. Aside from the correction factor which must be applied (to be discussed later), the thermopile output for many of the mercury-arc emission lines was very low, in the 0.01 to 0.1 microvolt range. Such low readings on the microvoltmeter were not always reproducible due to instrument drift. Evacuating and insulating the thermopile helped somewhat, but there was still some drift whether due to the thermopile or the voltmeter. Increasing the intensity of the light would be an obvious help, but this could not be done because then the photocurrent at some of the strong emission wavelengths would be off scale on the Cary electrometer. What was done during the latter part of the program was to obtain ratios of the intensities at the various wavelengths to the intensity at one wavelength, one with a fairly high intensity such as 265 or 365 millimicrons. Then during an experiment the intensity had to be measured only at the one wavelength. Comparing data obtained in this manner to data obtained measuring the intensity at all wavelengths shows the ratio method to be somewhat more consistent than the other.

E. Auxiliary Gas Handling System

In order to carry out work function determinations on the titanium-hydrogen and erbium-hydrogen systems as a function of hydrogen composition, it was necessary to provide a gas handling system through which known amounts of hydrogen could be added to the diode. This system (a modified Sieverts' apparatus) consists of a fore pump, mercury diffusion pump, manometer, McLeod Gauge, and gas burette. This glass system is connected to the diode vacuum system through a Granville Phillips low torque valve. Cold traps prevent mercury vapor from entering the diode system.

In an experimental run the following procedure was used: A known amount of titanium or erbium was evaporated from the tungsten heater on to the nickel substrate and the walls of the diode. After the work function of the evaporated metal was determined, the vac ion pump was closed off and the diode opened to the gas handling system. A known amount of hydrogen gas was added at room temperature. No difficulty was encountered in hydriding either titanium or erbium at room temperature. When the pressure dropped to a low value, the gas handling system was closed off from the diode. From the measured pressure and the known volume of the gas handling system, the residual amount of hydrogen was determined. The rest of the hydrogen was assumed to be absorbed uniformly by the titanium or erbium in the diode. Thus, the hydrogen composition of the film on the nickel substrate was determined. After the work function at that composition was determined, another batch of hydrogen was added and the procedure repeated.

F. Materials

The metals used in the photoelectric measurements were the same as those used in the thermionic work. Pertinent information is summarized in Table I.

The hydrogen gas used was obtained from the Cryogenic Laboratory of the Bureau of Standards. The oxygen and nitrogen impurity levels in this gas are estimated to be about one part per million. The most likely impurity is water vapor, but passing the gas through a silver-palladium leak removes any water vapor present.

TABLE I
SAMPLES

Material	Source	Diameter (inches)	Purity	Remarks
Titanium	Reactive Metals Inc.	0.025	99.7 to 99.8%	Spectrographic analysis* on the ingot Mg 20ppm, Cr 25ppm, Mn 20ppm, Sn 20ppm, Ni 60ppm, V 25ppm, Zn 50ppm, Ca 30ppm, Mo 20ppm. Chemical analysis* on 1/4 inch dia. bar .03%C, .01%N ₂ , .03%Fe, .02% Si, .093%O ₂ , 7 ppm H ₂ .
Titanium	Lyteess Metal Corp.	0.010	99.9%	
Vanadium	Lyteess Metal Corp.	0.010	99.7%	Mass Spectrographic analysis on wire** (all values ppm atomic) Fe 300, Cr 100, Ti 5, Ca 180, K 90, Cl 70, Si 400, Al 400, Na 900, O 1600, N 160, C 4000.
Chromium	Australian Aeronautical Research Labs.	0.019	99.99%	Spectrographic analysis** on wire Ni 20ppm, Na 3ppm, C 100ppm, O 100ppm.
Erbium	Bernard Ring, Inc.	0.020	99.+%	Mass Spectrographic analysis on wire** (all values ppm atomic) Ta 1200, Tm 550, Ho 150, Tb 25, Y 700, Ni 120, Cr 80, Ti 20, Mg 550. * Provided by the Supplier ** Analyzed by Sandia Corp.

III. FOWLER'S METHOD OF ANALYSIS OF PHOTOEMISSION DATA

At the turn of the century the photoelectric effect was one of a few rather obscure phenomena which could not be explained by classical theories. The elucidation of the effect in 1905 by Einstein and the subsequent experimental verification of Einstein's theory by Millikan and others substantiated the quantum theory of light, a very great and fundamental departure from classical theory. Einstein, expanding on Planck's original hypothesis that light is emitted and absorbed in a quantized manner, postulated that light can be considered to consist of quanta or photons of energy $h\nu$; h being Planck's constant and ν the frequency. He further postulated that the development of a photocurrent from an electrode in vacuum under the influence of light, that is, the photoelectric effect, resulted from the interaction of individual photons with the electrons in the electrode. The maximum energy of an emitted electron is then equal to the photon's energy $h\nu$ less the amount of work required to remove an electron from the electrode. This latter quantity, the work function, accounts for the fact that there is a threshold frequency ν_0 below which electrons are not ejected. That there is no absolutely discrete threshold frequency except at absolute zero will be discussed later, but for now suffice it to say that Einstein's theory accounted for all of the main features of the photoelectric effect.

A. Fowler's Theory

A complete theory of the photoelectric effect must account for the photoelectric yield, electrons emitted per photon absorbed, as a function of the frequency of the incident light and the temperature. Such a theory must take into account the following processes: photon absorption, photon-electron interaction (energy and momentum transfer) and electron emission. Fowler's theory is not a complete theory, but it accounts very well for the observed photoelectric yield at frequencies near the threshold frequency. Since the main purpose of this research was to determine photoelectric work functions or, in other words, threshold frequencies, Fowler's theory is most appropriate and adequate for these purposes.

Fowler* applied the Sommerfeld free electron theory of metals to the photoelectric effect. He took the photoelectric yield to be proportional to the number of electrons per unit volume of the metal "whose kinetic energy normal to the surface augmented by $h\nu$ is sufficient to

* Fowler, R. H., Phys. Rev. 38, 45 (1931).

overcome the potential step at the surface. " According to Fermi-Dirac statistics, which apply to a free electron gas, the number of electrons per unit volume with velocity components in the ranges v_x to $v_x + dv_x$, v_y to $v_y + dv_y$, and v_z to $v_z + dv_z$ is given by:

$$N(v_x, v_y, v_z) dv_x dv_y dv_z = 2 \left(\frac{m}{h} \right)^3 \frac{dv_x dv_y dv_z}{\exp \left\{ \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) - \mu_0 \right\} / kT + 1} \quad (1)$$

where μ_0 is the Fermi energy (the maximum kinetic energy of the electrons at absolute zero) and the other symbols have their usual meaning.* If v_x is normal to the surface, the number of electrons per unit volume with velocity components normal to the surface is given by:

$$N(v_x) dv_x = \int_{v_y} \int_{v_z} N(v_x, v_y, v_z) dv_y dv_z \quad (2)$$

$$N(v_x) dv_x = \frac{4\pi kT}{m} \left(\frac{m}{h} \right)^3 \ln \left\{ 1 + e^{(\mu_0 - \frac{1}{2} m v_x^2) / kT} \right\} dv_x \quad (3)$$

Fowler denotes the total height of the potential barrier at the boundary between metal and vacuum as χ_0 . Thus the difference between this energy and the Fermi energy, $\chi_0 - \mu_0 = h\nu_0$ where ν_0 is the threshold frequency, is the work function at absolute zero. Now the number of electrons per unit volume with velocity components normal to the surface and with sufficient kinetic energy to escape after the absorption of photons of energy $h\nu$ will be given by:

$$N = \int_{\frac{1}{2} m v_x^2 = \chi_0 - h\nu}^{\infty} N(v_x) dv_x \quad (4)$$

Making the substitution $y = \frac{1}{2} m v_x^2 - (\chi_0 - h\nu)$, and substituting for $N(v_x) dv_x$ as given in equation 3, this becomes:

$$N = \frac{2\pi kT}{m} \left(\frac{2kT}{m} \right)^{1/2} \left(\frac{m}{h} \right)^3 \int_0^{\infty} \frac{\ln \left\{ 1 + e^{(h\nu - h\nu_0) - y} / kT \right\}}{\{[y + (\chi_0 - h\nu)] / kT\}^{1/2}} dy \quad (5)$$

* This is an approximation: Actually the chemical potential μ rather than μ_0 appears in the equation. However, μ does not differ much from μ_0 at ordinary temperatures above absolute zero.

Fowler now argues that near the threshold, that is when $h\nu$ is not much different from $h\nu_0$, the y in the denominator of equation 5 can be neglected in comparison to $(\chi_0 - h\nu)$. Equation 5 thus becomes:

$$N = \frac{2^{3/2} \pi m^{3/2}}{h^3} \frac{k^2 T^2}{(\chi_0 - h\nu)^{1/2}} \int_0^\infty \ln \left\{ 1 + e^{\{(h\nu - h\nu_0) - y\}/kT} \right\} dy \quad (6)$$

The logarithm in equation 6 can be expanded and integrated term by term. The result is, for $(h\nu - h\nu_0)/kT = u \leq 0$:

$$N = \frac{2^{3/2} \pi m^{3/2}}{h^3} \frac{k^2 T^2}{(\chi_0 - h\nu)^{1/2}} \left[e^u - \frac{e^{2u}}{2^2} + \frac{e^{3u}}{3^2} - \dots \right] \quad (7)$$

and for $(h\nu - h\nu_0)/kT = u \geq 0$:

$$N = \frac{2^{3/2} \pi m^{3/2}}{h^3} \frac{k^2 T^2}{(\chi_0 - h\nu)^{1/2}} \left[\frac{\pi^2}{6} + \frac{1}{2} u^2 - \left\{ e^{-u} - \frac{e^{-2u}}{2^2} + \frac{e^{-3u}}{3^2} - \dots \right\} \right] \quad (8)$$

Fowler then assumes that the photoelectric yield Y is proportional to these numbers of electrons obtaining equations of the form:

$$Y = \frac{AT^2 f(u)}{(\chi_0 - h\nu)^{1/2}} \quad (9)$$

where A is a constant and $f(u)$ represent the infinite series contained in brackets in equations 7 and 8.

B. Method of Determining Work Functions from Fowler's Theory

Fowler further points out that near the threshold where $h\nu$ is not much different from $h\nu_0$, $(\chi_0 - h\nu)$ is practically constant. Under these conditions $(\chi_0 - h\nu)$ can be incorporated into the constant A . Dividing equation 9 by T^2 and taking the logarithm of both sides gives:

$$\log \frac{Y}{T^2} = B + \phi(u) \quad (10)$$

where $\phi(u) = \log f(u)$ and $B = \log A - \frac{1}{2} \log (\chi_0 - h\nu)$ and B is assumed to be a constant. The universal function $\phi(u)$ is tabulated by Du Bridge* for both $u \geq 0$ and $u \leq 0$. A plot of $\phi(u)$ vs. u is presented in Figure II.

* Du Bridge, L. A., Phys. Rev. 39, 108, (1932).

Figure II. Fowler's Theoretical Curve

From experimental data one determines Y at a constant temperature as a function of the frequency of light ν near the threshold frequency ν_0 . One then plots $\log Y/T^2$ vs. $h\nu/kT$ and compares this plot to a plot of $\phi(u)$ vs. u , $u = (h\nu_0 - h\nu)/kT$. If the experimental curve is made to coincide with the theoretical curve, one sees from equation 10 that the horizontal shift yields $h\nu_0/kT$ and the vertical shift yields B . Thus one obtains the threshold frequency ν_0 .

That there is no sharp cutoff in yield at ν_0 is obvious from Fowler's theoretical curve where $\phi(u)$ remains a smooth function for values of $h\nu$ less than $h\nu_0$. Recall that $h\nu_0$ was defined by Fowler as the difference between the total height of the potential barrier and the Fermi Energy, $\chi_0 - \mu_0$. Thus the $h\nu_0$ determined by Fowler's method is by definition the work function at absolute zero. Du Bridge* calls this a "true" work function, and points out its independence of the temperature. It should be recalled however, a point not mentioned by Du Bridge, that an approximation has been made, albeit a good one, that $\mu = \mu_0$ at temperatures above absolute zero.

C. Anderson's Approximation to Fowler's Equation

Anderson** seems to have been the first to recognize that by dropping small terms from the infinite series in Fowler's equation, the equation takes on a particularly simple form. Going back to equation 9, and writing out the first few terms of $f(u)$:

$$Y = \frac{AT^2}{(\chi_0 - h\nu)^{1/2}} \left\{ \frac{\pi^2}{6} + \frac{1}{2}u^2 - \left[e^{-u} - \frac{e^{-2u}}{2^2} + \frac{e^{-3u}}{3^2} \dots \right] \right\} \quad (11)$$

Taking $u^2/2$ out of the brackets gives:

$$Y = \frac{AT^2u^2}{2(\chi_0 - h\nu)^{1/2}} \left\{ 1 + \frac{\pi^2}{3u^2} - \frac{2}{u^2} \left[e^{-u} - \frac{e^{-2u}}{2^2} + \frac{e^{-3u}}{3^2} \dots \right] \right\} \quad (12)$$

By setting the u^2 which multiplies the brackets equal to $(h\nu - h\nu_0)^2/k^2T^2$ and letting $A = k^2C$, equation 12 becomes:

$$Y = \frac{C(h\nu - h\nu_0)^2}{2(\chi_0 - h\nu)^{1/2}} \left\{ 1 + \frac{\pi^2}{3u^2} - \frac{2}{u^2} \left[e^{-u} - \frac{e^{-2u}}{2^2} + \frac{e^{-3u}}{3^2} \dots \right] \right\} \quad (13)$$

* Ibid.

** J. S. Anderson, E. A. Faulkner, and D. F. Klemperer, Aust. J. Phys., 12, 469 (1959).

Obviously when $u \gg 1$, this reduces to:

$$Y = \frac{C(h\nu - h\nu_0)^2}{2(\chi_0 - h\nu)^{1/2}} \quad (14)$$

Taking the square root of both sides gives:

$$Y^{1/2} = \frac{C^{1/2}(h\nu - h\nu_0)}{2^{1/2}(\chi_0 - h\nu)^{1/4}} \quad (15)$$

If, then, $(\chi_0 - h\nu)$ is practically constant, as is assumed in Fowler's theory for frequencies near the threshold, a plot of $Y^{1/2}$ vs. $h\nu$ will be linear, and $h\nu_0$ will be equal to the value of $h\nu$ where $Y^{1/2}$ equals zero.

The $Y^{1/2}$ vs. $h\nu$ plot, what is called here the Anderson approximation, has proved in this research to be very useful and in complete agreement with results obtained from Fowler plots. At first look it would appear that contradictory assumptions are made in making the Anderson approximation. In the first place the Fowler theory applies only when $h\nu$ is near the threshold energy $h\nu_0$, in which case y can be neglected in the denominator of the integral in equation 5 and, in addition $(\chi_0 - h\nu)$ can be considered practically a constant. On the other hand, in order to drop all terms but the first (equal to one) contained in the brackets in equation 13, u must be much greater than one, implying that $h\nu \gg h\nu_0$. Numerical analysis, however, shows that there is really no contradiction here. Considering values of $h\nu$ between zero and about one electron volt greater than $h\nu_0$ (in this range the deviation caused by changes in $\chi_0 - h\nu$ are less than 5%) one finds that as $h\nu$ gets larger, even in this limited energy range, u increases very rapidly. For example, for some data which showed a work function of 3.30 eV, the first data point above the threshold was at 3.4 eV, at which point u is equal to 3. The next point was at 3.71 eV where u is equal to 16; and the third point was at 3.96 eV where u is 25. Thus, u does increase quite rapidly, but this does suggest that the first couple of data points above threshold should be considered with some suspicion.

IV. NUMERICAL ANALYSIS OF PHOTOELECTRIC-EMISSION DATA

A. Correction Factors

In order to determine absolute yields of photoelectrons per absorbed photon, the recorded data must be corrected for absorption and reflection in the light path. In determining the photocurrent the light passes through a quartz window on the arm of the high vacuum chamber. A scanning spectrophotometer (available in the Chemistry Division of the Denver Research Institute) was used to determine the combined absorptivity-reflectivity of the quartz window from 220 millimicrons to 900 millimicrons. A scan was made with nothing in the light beam, and then repeated with the quartz window in the beam. From this double scan, intensity ratios were calculated for those wavelengths which correspond to emission lines in the Hg-arc spectrum. The results are presented in the second column of Table II.

A front surface aluminized mirror is used to divert the light from the monochromator to the thermopile. Intensity measurements for the Hg-arc emission lines were made with and without the mirror. Average intensity ratios were determined and are given in column three of Table II.

As is mentioned previously, a modification in the method of determining intensities of the emission lines was introduced about half way through the program. It was felt that the difficulty in measuring the intensities of the weaker lines was causing unnecessary scatter in the data. Intensity ratios were determined for all the emission lines to the strong line at 365 millimicrons. The thermopile was placed directly in front of the monochromator to get maximum output. A number of intensity readings were made at each wavelength. After each reading at a particular wavelength, a reading at 365 millimicrons was made, and the ratio of the intensity at 365 millimicrons to that at the other wavelength was determined. Although the absolute intensities varied somewhat from one set of readings to another, the ratios turned out to be quite reproducible. The ratios were converted to ratios of the intensity of the 265 millimicron line to the other lines and these ratios are presented in the fourth column of Table II. The ratios were used as follows. In an experimental run the intensity of the 265 millimicron line was measured. The mirror correction, in this case a multiplication of the measured value by 1.21, was made, and the intensities of the other lines were calculated from the ratios. In all of the experimental runs the

TABLE II

CORRECTION FACTORS AND INTENSITY RATIOS FOR REDUCTION
OF PHOTOELECTRIC EMISSION DATA

<u>Wavelengths</u> <u>(millimicrons)</u>	<u>Intensity Ratios</u>		
	<u>no window</u> <u>window</u>	<u>no mirror</u> <u>mirror</u>	<u>265 mμ line</u> <u>other lines</u>
226	1.23	1.30	15.8
231	1.25	1.28	12.3
239	1.31	1.27	5.83
248	1.26	1.24	2.86
253	1.20	1.23	1.51
265	1.12	1.21	1.00
270	1.12	1.20	5.03
275	1.11	1.20	6.96
280	1.11	1.19	2.16
289	1.11	1.19	3.75
297	1.11	1.19	--
302	1.11	1.19	0.759
313	1.10	1.19	0.319
334	1.10	1.19	2.69
365	1.10	1.19	0.217
393	1.10	1.10	--
404	1.09	1.10	0.813

intensities of all the lines actually were measured. Thus, the two methods (direct measurement and the use of ratios) could be compared. Generally the ratio method gave a better fit to the theoretical curves.

Another correction which should be made is for the absorptivity-reflectivity of the thin quartz window on the thermopile. The thermopile was calibrated using polychromatic light and a correction factor applied for the effect of the window. This correction factor, 1.1, has been used in reducing the data, but it has been assumed to be the same for all wavelengths, which it is not. It should be pointed out, however, that the small corrections being discussed here have little effect on the determination of work functions. Neither the Fowler plot nor the Anderson plot are particularly sensitive to these small corrections.

B. Reduction of Experimental Data

In photoelectric emission studies the experimental quantity of primary interest is the photoelectric yield: the number of photoelectrons emitted per photon absorbed at each different wavelength of light employed. This ratio of electrons per photon which will henceforth be denoted by Y , is determined from the experimental data as follows: The photocurrent is measured by the Cary electrometer. The output of this instrument is in volts, and the resistance of the instrument is 10^{11} ohms. Thus, the photocurrent in amps is given by the measured voltage divided by 10^{11} ohms. Dividing this quantity by the area of the slit image on the photocathode gives amps per cm^2 . One amp is one coulomb per sec, and the charge on one electron is 1.60206×10^{-19} coulombs. Therefore, the number of electrons per cm^2 per sec is given by:

$$\text{electrons/cm}^2\text{-sec} = \frac{\text{Measured Photovoltage in volts}}{(10^{11} \text{ ohms})(\text{area of slit image})(1.60206 \times 10^{-19} \text{ coulombs/electron})}$$

To determine the number of photons per cm^2 per sec striking the cathode the thermopile output is converted as follows: The output of the thermopile is in microvolts; the calibration in polychromatic light with the quartz window in place gave 0.055 microvolts per microwatt/ cm^2 . Using this conversion at all wavelengths assumes that the absorption of the thermopile and the absorption of the quartz window are the same at all wavelengths. The former assumption may be valid, but the latter is not, and thus, small errors are introduced as has been mentioned in the previous section. Dividing the measured thermopile output by 0.055 gives microwatts per cm^2 . Multiplying this by 10^{-6} watts per microwatt

and by 10^7 ergs per watt-sec gives erg per cm^2 per second. Dividing this by the number of ergs per photon at each particular wavelength hc/λ , where h is Planck's constant, c is the speed of light, and λ is the wavelength in cm, gives the desired result: photons per cm^2 per second.

Thus:

$$\text{photons/cm}^2\text{-sec} = \frac{(\text{Thermopile output in } \mu\text{-volts} \times 10^{-6} \text{ watts}/\mu\text{-watt}) (10^7 \text{ ergs/watt-sec})}{(0.055 \mu\text{-volt}/\mu\text{-watt per cm}^2) (hc/\lambda \text{ ergs/photon})}$$

and the yield, Y , is given by:

$$Y = \frac{\text{electrons/cm}^2\text{-sec}}{\text{photons/cm}^2\text{-sec}} = \frac{\text{Measured Photovoltage in volts} \times K}{\text{Measured Thermopile output in } \mu\text{-volts} \times \text{area of slit in cm}^2 \times \lambda \text{ in cm}}$$

where

$$K = \frac{0.055 \times 6.625 \times 10^{-27} \times 2.99793 \times 10^{10}}{10^{11} \times 1.60206 \times 10^{-19} \times 10^{-6} \times 10^7}$$

$$K = 6.82 \times 10^{-11}$$

In Tables III and IV are presented a complete set of data for one run. This particular run was on the nickel substrate before the evaporation of titanium. The results of this experiment will be discussed later; the data are given here as an example of how the data were reduced. Since there were well over one-hundred runs made in the course of this work, in this report detailed tables such as this will not be presented except in this case.

In Table III the yield Y is calculated using measured light intensity at all wavelengths. In Table IV the yield is based on the intensity ratios discussed above. A Fowler plot of these data is presented in Figure III. In this figure the dots represent the data from Table III and the x's the data from Table IV. As can be seen, the x's provide a better fit to the theoretical curve than do the dots.

To determine the work function from the $\log Y/T^2$ vs. $h\nu/kT$ plot, one superimposes the theoretical Fowler curve (Figure II) on the experimental points and draws the theoretical curve that best fits the points. This has been done in Figure III. One then observes the shift along the horizontal axis that would make the two curves coincide. As has been

TABLE III

PHOTOELECTRIC EMISSION DATA FOR Ni SUBSTRATE (RUN #93)

Wavelength ($\text{cm} \times 10^5$)	Photocurrent (volts)	Correction Factor for Quartz Window	Corrected Photocurrent (volts)	Thermopile Output (μ -volts)
2.26	0.80	1.23	0.984	0.09
2.31	0.98	1.25	1.225	0.12
2.39	1.33	1.31	1.74	0.16
2.48	1.83	1.26	2.31	0.32
2.53	2.72	1.20	3.26	0.54
2.65	2.03	1.12	2.27	0.90
2.70	0.229	1.12	0.256	0.24
2.75	0.103	1.11	0.114	0.19
2.80	0.141	1.11	0.157	0.50
2.89	0.0073	1.11	0.0081	0.31

Correction Factor for Mirror	Corrected Thermopile Output (μ -volts)	Area of Slit Image (cm^2)	Photocurrent divided by Thermopile $\times$ area $\times$ wave- length (Y/K) $K=6.82 \times 10^{-11}$	Y ($\frac{\text{electrons}}{\text{photon}}$)	Log Y
1.30	0.117	0.95	3.92×10^5	2.67×10^{-5}	-4.573
1.28	0.154		3.62×10^5	2.47×10^{-5}	-4.607
1.27	0.203		3.78×10^5	2.59×10^{-5}	-4.589
1.24	0.397		2.46×10^5	1.68×10^{-5}	-4.274
1.23	0.664		2.04×10^5	1.40×10^{-5}	-4.856
1.21	1.09		8.26×10^4	5.64×10^{-6}	-5.248
1.20	0.288		3.46×10^4	2.36×10^{-6}	-5.627
1.20	0.228		1.92×10^4	1.31×10^{-6}	-5.883
1.19	0.595		9.89×10^3	6.75×10^{-7}	-6.171
1.19	0.369		8.0×10^2	5.46×10^{-8}	-7.263

$\text{Log } (Y/T^2)$ ($T=298^\circ\text{K}$)	$h\nu$ (eV)	$\frac{h\nu}{kT}$ ($T=298^\circ\text{K}$)	$Y^{1/2}$ ($\frac{\text{electron}}{\text{photon}}$) $^{1/2}$
-9.521	5.49	214	5.15×10^{-3}
-9.555	5.37	209	4.96×10^{-3}
-9.537	5.19	202	5.06×10^{-3}
-9.722	5.00	195	4.09×10^{-3}
-9.804	4.91	191	3.73×10^{-3}
-10.196	4.68	183	2.37×10^{-3}
-10.575	4.59	179	1.53×10^{-3}
-10.831	4.51	176	1.14×10^{-3}
-11.119	4.43	173	8.21×10^{-4}
-12.211	4.29	167	2.33×10^{-4}

TABLE IV

PHOTOELECTRIC EMISSION DATA FOR Ni SUBSTRATE (RUN #93) BASED ON INTENSITY RATIOS

Wavelength ($\text{cm} \times 10^5$)	<u>Intensity 265 mμ line</u> <u>Intensity other lines</u>	Thermopile Output* (μ -volts)	Y ($\frac{\text{electrons}}{\text{photon}}$)	Log Y	Log Y/T ² (T=298°K)	Y ^{1/2}
2.26	15.8	0.069	4.53×10^{-5}	-4.344	- 9.294	6.72×10^{-3}
2.31	12.3	0.089	4.29×10^{-5}	-4.368	- 9.316	6.54×10^{-3}
2.39	5.83	0.187	2.79×10^{-5}	-4.554	- 9.502	5.27×10^{-3}
2.48	2.86	0.381	1.75×10^{-5}	-4.757	- 9.705	4.18×10^{-3}
2.53	1.51	0.722	1.28×10^{-5}	-4.892	- 9.840	3.58×10^{-3}
2.65	1.00	1.09	5.64×10^{-6}	-5.248	-10.196	2.37×10^{-3}
2.70	5.03	0.217	3.13×10^{-6}	-5.504	-10.452	1.77×10^{-3}
2.75	6.96	0.157	1.90×10^{-6}	-5.721	-10.669	1.38×10^{-3}
2.80	2.16	0.504	7.97×10^{-7}	-6.198	-11.146	8.91×10^{-4}
2.89	3.75	0.291	6.92×10^{-8}	-7.160	-12.108	2.63×10^{-4}

* Note that these values are based on the intensity ratios and one thermopile reading at 265 millimicrons which when corrected for the reflectivity of the mirror was 1.09 μ -volt, see Table III.

Figure III. Fowler Plot of Data for Nickel Substrate

discussed previously, this shift is equal to $h\nu_0/kT$. The shift for Figure III is 168 units. This corresponds to a threshold wavelength of 287 millimicrons and to a work function of 4.32 eV.

In Figure IV are presented the $Y^{1/2}$ vs. $h\nu$ plots for the data of Tables III and IV (Run #93), again dots and x's respectively. Again it is seen that the x's give a better fit to the straight line. The work function from this plot is very simply obtained from the intercept of the line and the $Y^{1/2} = 0$ axis. For Run #93 it is seen to be 4.29 eV.* This value agrees within 0.03 eV with the value from the Fowler plot. It should be pointed out that a shift of one unit to the left on the Fowler plot would correspond to a decrease in work function of 0.03 eV, and the two work functions would be identical. Such a shifted curve on the Fowler plot would equally well fit the experimental points as the curve drawn in Figure III. Agreement of this kind was generally found in comparing the two methods. Thus the exclusive use of the Anderson ($Y^{1/2}$ vs. $h\nu$) plot in the latter part of the program was justified.

* In Figure IV the intercept of the line with the $Y^{1/2} = 0$ axis is shown to be 4.285 eV. This represents the precision with which the intercept could be determined; it does not represent the accuracy with which work functions were determined. In practice the data from several experimental runs for the same material were plotted on the same graph. A visual estimate could then be made of the uncertainty of the intercept. The uncertainty was always less than ± 0.1 eV and in many cases less than this. Uncertainty limits given in the text are based on this visual observation.

Figure IV. $Y^{1/2}$ vs. $h\nu$ Plots for Ni and Ti

V. RESULTS AND DISCUSSION

A. Nickel

As has been discussed previously nickel was the substrate upon which the other metals of interest in this program were evaporated. In all but the first experiments with titanium films the work function of the nickel substrate was determined before depositing the film. The nickel used was greater than 99.9% pure and was cleaned with dilute nitric acid and distilled water before being positioned in the vacuum chamber.

Typical data for the first experiments carried out on nickel are presented in Figures III and IV (Run #93) in the previous section. These data were taken at a pressure of 1.4×10^{-8} mm of Hg after the system had been baked out with heating tapes. The work function value obtained from these data, that is, 4.30 eV, is somewhat lower than most of the thermionic and photoelectric work function values for polycrystalline nickel reported in the literature.* It was thought that there might have been some preferred orientation in the sample with a low work function crystal face in preponderance. An X-ray diffraction pattern from a sample of nickel from the same batch as that in the diode did not show preferred orientation.

This same nickel sample was heated with an induction coil prior to depositing a titanium film. The intent was to clean the nickel surface thereby increasing the adherence of the Ti film. A thermocouple attached to the nickel indicated that the maximum temperature reached was about 340°C. Photoemission data taken after this heat treatment showed very clearly that the work function had increased. A $\gamma^{1/2}$ vs $h\nu$ plot of one set of data is shown in Figure IV (Run #96). From this plot the work function is seen to be 4.54 eV. This demonstrates the great sensitivity of work function values to adsorbed surface films. Such changes in work function values in various environments are called surface potentials. Thus the surface potential on the nickel before heat treatment was -0.24 eV. This can be interpreted to mean that whatever was adsorbed on the nickel was positively charged.

The work function value of 4.54 eV obtained in Run #96 and confirmed by other runs is very close to the value of 4.50 eV recommended by Fomenko and Samsonov.**

* V. S. Fomenko, "Handbook of Thermionic Properties," Edited by G. V. Samsonov, Plenum Press Data Division, New York, 1966.

**Ibid.

The nickel sample discussed above was used as the substrate in a series of experiments with titanium and the titanium-hydrogen system. At the conclusion of these experiments the system was disassembled, cleaned, and reassembled in preparation for experiments with erbium and the erbium-hydrogen system. The same nickel sample, after cleaning with NH_4HF_2 solution and distilled water, was replaced in the diode. After bake-out of the system but no further heat treatment of the nickel sample its work function was determined. A Fowler plot of the data gives a work function of 4.49 eV, and a $Y^{1/2}$ vs $h\nu$ plots gives 4.52 eV. These values are in good agreement with the value of 4.54 eV obtained previously after heat treatment.

Subsequent to the erbium experiments the nickel sample was removed, this time cleaned with dilute nitric acid and distilled water, and replaced for another series of experiments with erbium and the erbium-hydrogen system. After the system was baked out the photocurrent from the nickel substrate was found to be much lower at all wavelengths than it had been in previous experiments. This was no doubt due in part to the fact that the intensity of the mercury arc was less than it had been; in fact the arc burned out shortly after these attempts to measure photocurrents were made. It was thought at the time that the lowered current might be due to a high positive surface potential caused by adsorbed material on the nickel surface. Consequently the nickel sample was induction heated to a temperature of 640°C . After this heat treatment, and using a new mercury arc, the work function was determined to be 4.80 eV. Why the work function was higher after the 640°C heat treatment than it was after the 340°C heat treatment is not known. This again points out the great sensitivity of work functions to surface contaminants.

Another nickel sample, after cleaning with nitric acid and water, was used as the substrate for experiments on vanadium. The work function of the nickel, with no heat treatment except bake out of the system, was determined to be 4.50 eV. It can be concluded that whatever caused the work function to increase in the previous experiments was no longer present in these experiments. It can furthermore be concluded that the photoelectric work function of clean, polycrystalline nickel is 4.50 eV plus or minus about 0.05 eV.

B. Titanium

In the early part of this research program a piece of sheet titanium, the same size as the nickel substrate used subsequently, was used

as the photoemitter in many experiments carried out to check out the equipment and the experimental procedures. Many photoemission measurements were made using this emitter; the precision of the data improving with experience. The work function determined from all of these data was in the range from 3.97 to 4.10 eV. A $\gamma^{1/2}$ vs $h\nu$ plot of the data from one run is shown in Figure V. The work function from these data is seen to be 3.97 eV. A work function value in this range is in good agreement with photoelectric work functions reported in the literature* for polycrystalline titanium.

The work function of evaporated titanium films was found to be considerably lower than that of the sheet titanium discussed above. Titanium was evaporated onto the nickel substrate at an initial pressure of 1×10^{-9} mm of Hg. As has been previously mentioned, the evaporation was not done at once, but was carried out in a stepwise manner so as not to overheat the diode. During each step the pressure in the system increased, and then decreased as the heating wire and the titanium cooled. The final pressure was again 1×10^{-9} mm of Hg. Photoemission data taken immediately after evaporation were erratic as can be seen in Figure V. It is difficult to draw a line through the points on this $\gamma^{1/2}$ vs $h\nu$ plot, but the suggestion is that the work function is of the order of 3.8 eV. Some days after evaporation good, reproducible data were obtained, and the results of one run are shown in Figure V. As can be seen these data give a work function of 3.52 eV. The same work function was obtained from a Fowler plot.

A second titanium film, prepared in the same manner and under the same conditions as the one described above, yielded a work function of 3.60 eV (see Run #104 in Figure IV). In this case also there was a suggestion that the work function decreased with time immediately after evaporation.

The thermionic, Richardson work function determined in this research program (see DRI Summary Report #2344) for the same titanium wire was 3.77 eV. Wilson** reports a temperature dependent, effective, thermionic work function for β -titanium of from 3.6 to 4.3 eV. Because of the temperature dependence of the thermionic work function, a comparison of such work functions with photoelectric work functions obtained at room temperature is not really justified. It can be concluded, however,

* Ibid.

** R. G. Wilson, J. Appl. Phys., 37, 2261 (1966).

Figure V. $Y^{1/2}$ vs. $h\nu$ Plot for Evaporated and Sheet Titanium

that the work function of clean, freshly evaporated films of titanium is considerably lower than the work functions of titanium surfaces that have been exposed to the atmosphere.

C. The Titanium-Hydrogen System

Two experimental runs were made on the titanium-hydrogen system over a period of several months. Hydrogen was added at room temperature in a batch-wise manner to the system after titanium had been evaporated, and the composition of the hydride was calculated from the known amount of titanium in the system and the amount of hydrogen absorbed. In the first run the work function of the titanium film before hydrogen was added was 3.52 eV (see above). The first batch of hydrogen added resulted in a composition $\text{TiH}_{0.049}$. The data obtained in one run on this material are shown as circles in Figure VI. As can be seen, this amount of hydrogen reduced the work function from 3.52 to 3.30 eV.

Additional batches of hydrogen were added as indicated in Figure VI, bringing the composition up to $\text{TiH}_{0.4}$. The slopes of the $Y^{1/2}$ vs $h\nu$ plots varied somewhat with composition, but the work functions remained essentially constant. All of the data fell within the extremes indicated in Figure VI, giving a work function of 3.30 ± 0.03 eV. When the composition had reached $\text{TiH}_{0.4}$, it was observed that the hydride film on the nickel substrate and on the walls of the diode was beginning to flake off. The next addition of hydrogen caused more flaking, and it appeared that the entire film had flaked off the nickel substrate. However, a work function measurement did not give the work function of nickel, but gave a value the same as that observed for the composition $\text{TiH}_{0.4}$. It was concluded that there was still an integral hydride film on the nickel substrate. It should be recalled that the titanium film was deposited in four or five evaporation steps. When hydrided to composition $\text{TiH}_{0.4}$, some of the layers flaked off but not all. Probably what remained was the film from the first evaporation.

It was decided at this point to hydride the remaining film to the maximum hydrogen composition to see if there would be any further change in work function. Hydrogen was added sufficient to bring the composition up to TiH_2 and left for several days. The final pressure was 3.5 mm of Hg. The excess hydrogen was pumped out of the system and the final composition was calculated to be $\text{TiH}_{1.62}$. The work function determined for this composition was 3.31 eV from a $Y^{1/2}$ vs $h\nu$ plot and 3.32 eV from a Fowler plot. It was concluded, therefore, that the work function of titanium hydride films varying in composition from $\text{TiH}_{0.5}$ to $\text{TiH}_{1.62}$ is 3.30 ± 0.03 eV and is independent of composition over this range.

Figure VI. $Y^{1/2}$ vs. $h\nu$ Plots for Titanium Hydrides of Various Compositions

The hydride remaining on the nickel substrate as well as some of the hydride that had flaked off the walls of the diode were sent to Sandia for analysis. The flaked off material showed a hydrogen to titanium ratio of from 1.40 to 1.45. The ratio for the hydride on the nickel substrate was 1.63, in excellent, if perhaps fortuitous, agreement with the calculated ratio of 1.62. From the weight of the film on the nickel, 194 micrograms, the thickness of the film was calculated to be about 670 Å.

In the second experimental run on the titanium-hydrogen system the work function of the evaporated titanium film before hydrogen addition was 3.60 eV (see discussion of titanium above). In this run the hydrogen was added in very small batches. This was done in an attempt to determine at what composition the work function is reduced to the value of 3.3 eV observed in the previous experiments after the first addition of hydrogen to give a composition $\text{TiH}_{0.05}$. The first four batches of hydrogen added resulted in the compositions $\text{TiH}_{0.003}$, $\text{TiH}_{0.006}$, $\text{TiH}_{0.01}$, and $\text{TiH}_{0.013}$. At first it was thought that these small additions of hydrogen had no effect on the work function of the titanium; at least no perceptible change in work function within the scatter of the data points. However, when the data for these compositions are plotted together, as is done in Figure VII, a definite trend becomes apparent. The points at the upper right fall lower and lower as hydrogen is added, while the points at the lower left fall higher and higher with increasing hydrogen content. The only exception to this is the case of the data for the composition $\text{TiH}_{0.013}$ which falls below the data for the composition $\text{TiH}_{0.01}$ in the lower left of the figure. Because of this trend towards lower work functions as hydrogen content increases, it was felt justified to draw separate lines for the data at each composition despite the scatter in the points. This could not be done, however, for the data at the higher two compositions because of the anomaly mentioned above, and only one line is drawn representing these compositions.

From Figure VII it is seen that the first addition of hydrogen reduced the work function from 3.60 to 3.58 eV; the second batch reduced it further to 3.55 eV; and the third and fourth batches reduced it still further to 3.48 eV. After the fifth batch of hydrogen was added to bring the composition to $\text{TiH}_{0.016}$ the mercury arc burned out before photoemission data could be taken. The system remained at this composition for several days awaiting a new arc. When the new arc was installed and data taken, it was very surprising to find that the work function had increased to about 4.0 eV. It was felt at this time that in some manner the emitter surface had become contaminated during the many days that it remained at one composition without pumping. A large batch of

Figure VII. $Y^{1/2}$ vs. $h\nu$ Plots for Ti-H System

hydrogen was added, enough to bring the composition to $\text{TiH}_{1.29}$, but after three days only enough gas was absorbed to bring the composition to $\text{TiH}_{0.231}$. The work function was now found to be 4.62 eV, close to the value for the nickel substrate. When the system was disassembled, it was observed that the hydride film had flaked off the nickel substrate. This would explain the high work function value obtained.

From the results of these experiments the following conclusions can be drawn: When small amounts of hydrogen are added to titanium the work function decreases as the hydrogen content increases. Somewhere in the composition range from $\text{TiH}_{0.013}$ to $\text{TiH}_{0.05}$ the work function reaches a limiting value of 3.30 eV. Over the composition range from $\text{TiH}_{0.05}$ to $\text{TiH}_{1.62}$ the work function remains 3.30 eV.

D. Erbium

Erbium metal was evaporated onto the nickel substrate in the same manner as that employed for titanium. Two evaporations were made prior to hydriding experiments, and photoemission measurements were made on the freshly evaporated erbium films. The work function determined in the first experiment was 3.10 ± 0.05 eV and that from the second experiment was 2.75 ± 0.05 eV. Both evaporations were carried out in the same manner under very high vacuum conditions. Thus, there are no obvious reasons for the significant difference in the two work functions determined. In the thermionic experiments carried out for erbium wires (the same material as that used in the photoelectric experiments) Richardson work functions of 3.10 ± 0.04 and 3.11 ± 0.09 eV were determined in two separate measurements. In both cases, X-ray diffraction patterns showed the presence of erbium oxide on the surface of the wires. In one thermionic experiment, the emission current density changed with time after the erbium wire was heated. After about 24 hours the current stabilized and the work function was determined to be 3.10 eV. However, measurements made before stabilization of the current indicated a lower work function. The indications are, then, that the value of 3.10 eV is representative of erbium oxide while the work function of clean metal is lower.

A possible interpretation of the photoelectric results is that the first evaporated film in some manner became contaminated with oxide while the second film did not. It is felt, therefore, that the lower value, 2.75 eV, is more representative of clean erbium metal than the value of 3.10 eV.

E. The Erbium-Hydrogen System

Hydrogen was added in a batchwise manner to form erbium hydrides of varying compositions in the same manner as was employed in studying the titanium-hydrogen system. The first erbium film studied was that mentioned above which had a work function of 3.10 eV before hydrogen was added. The first hydrogen addition resulted in a composition of $\text{ErH}_{0.0065}$. The work function determined for this composition was the same as that for erbium metal. Further hydrogen additions were made resulting in hydrogen to erbium ratios of 0.012, 0.0185, 0.0254, 0.0329, 0.0387, 0.0993, 0.154, 0.198 and 0.250. While there is a considerable scatter in the data, and the slopes of the $\gamma^{1/2}$ vs. $h\nu$ plots change from one set of data to another, there is no evidence at any of these compositions that the work function, that is, the intercept of the line with the $\gamma^{1/2}$ equal zero axis, has changed from that of the original metal surface. This is in contrast with the results obtained for the titanium-hydrogen system where the work function decreased with hydrogen content and leveled off at a value about 0.25 eV lower than that of the metal.

The next batch of hydrogen added brought the composition up to $\text{ErH}_{0.2996}$. Three sets of data taken at this composition are consistent with a work function of 3.18 eV, a value slightly higher than that of the metal or of the other hydrogen compositions studied. At this time a crack developed in the view port of the high vacuum diode admitting air to the system. The erbium hydride film was contaminated and no further experiments could be carried out on this film.

The second series of experiments on the erbium-hydrogen system were carried on the erbium film which showed a work function of 2.75 eV. The first batch of hydrogen added resulted in the composition $\text{ErH}_{0.252}$. The work function at this composition was essentially the same as for the metal film. Additional batches of hydrogen were added resulting in hydrogen to erbium ratios of 0.502, 0.7539, 1.00, and 1.25. At all these compositions the work function was 2.75 eV.

The next batch of hydrogen brought the composition up to $\text{ErH}_{1.45}$, and there was a corresponding increase in work function to 3.20 eV. At this time it was observed that the erbium hydride film was beginning to flake off the nickel substrate. The work function remained 3.20 eV for a composition $\text{ErH}_{1.754}$, but for a composition of $\text{ErH}_{1.99}$ a further increase in work function to 3.70 eV was observed. It was also observed at this time that almost all of the dark hydride film had flaked off the nickel substrate. In the first experiments on the titanium-hydrogen system most of the

hydride film flaked off the substrate, but a thin film was retained as was subsequently shown by analysis. On the chance that this was the case also for erbium, the experiments were continued. Hydrogen additions resulting in hydrogen to erbium ratios of 2.24, 2.488, 2.75, and 3.01 were made. The work function remained 3.70 eV at all these compositions.

The final work function of 3.70 eV is far below that of the nickel substrate, which probably means that a hydride film remained after most of the hydride flaked off. On the other hand it could be that the light beam impinged on both hydride and nickel resulting in an apparent work function intermediate in value between the values for the two materials. It can certainly be concluded from the results of these two runs that hydrogen contents corresponding to hydrogen to erbium ratios of one or less do not change the work function of the surface from that of the original metal.

F. Vanadium

Vanadium was evaporated onto the nickel substrate in the same manner as was employed for titanium and erbium. Three separate sets of photoemission data were taken at different times after evaporation. The three $Y^{1/2}$ vs $h\nu$ plots are all consistent with a photoelectric work function of 4.07 ± 0.05 eV. The thermionic, Richardson work function obtained in this work was 4.66 ± 0.05 eV. The photoelectric value is closer in magnitude to a thermionic work function of 4.12 eV reported by Krishnan and Jain.* In the Fomenko compilation (see page 23 for reference) values for the work function of vanadium are given which range from 3.77 to 4.44 eV. Not all the values given represent actual determinations, many are taken from review papers or other compilations and are repeat values or estimates. It appears that besides the work described in this report, one other photoelectric work function value for vanadium has been measured. The value 3.77 eV was reported by Schulze** in 1934. In view of the purity of the starting material and the high vacuum conditions employed in the work reported here, it is felt that the value obtained in this work, 4.07 ± 0.05 eV, should be accepted as the most accurately determined photoelectric work function of vanadium.

* K. K. Krishnan and S. J. Jain, Proc. Roy. Soc. (London) A215, 431 (1952)

** R. Schulze, Z. Phys., 92, 212 (1934)

G. Chromium

Chromium was evaporated onto a nickel substrate in the same manner as was employed for the other metals. In this case, and only in this case, a good, adherent film was not obtained. Several hours after the evaporation the film appeared to be wrinkled. It was also observed that some of the film had flaked off the substrate. In taking data the image size was adjusted so that the image did not fall on an area where chromium had flaked off.

The first emission measurements on chromium were made shortly after the film had been deposited. The emission current was small in comparison to what had been observed from films of other materials. The best line through the data points obtained in this measurement gave a work function of 4.83 eV.

Following this first measurement no emission current could be obtained from the chromium film. Equipment failure was suspected, particularly the electrometer, and all items were checked out. No definite malfunctions were uncovered. Finally the tungsten heater, used originally to evaporate the chromium, was repeatedly flashed in an effort to heat-treat the chromium film. Following this heat-treatment, detectable current, although very weak, was obtained, and another run was made. These data gave a work function of about 4.55 eV.

Following this run again no emission current could be obtained. Another heat-treatment with the tungsten heater failed to produce detectable current. The substrate and film were removed from the system and observed. Some of the chromium film had flaked off the nickel substrate, but only a very small amount of nickel was exposed over the region where the image of the light beam impinged. Thus it was concluded that the surface being studied was predominantly chromium and not nickel.

It is unfortunate that the value of 4.55 eV could not be confirmed in several experimental runs. However this value is in agreement with values for chromium reported in the literature. Fomenko's compilation gives photoelectric work function values from 3.72 to 4.51 eV, and thermionic work function values from 4.51 to 4.70 eV. The thermionic work function determined in this study was 4.42 ± 0.07 eV. Work functions determined by contact potential difference measurements range from 4.38 to 4.63 eV. Fomenko's recommended value is 4.58 eV.

Thus, the value of 4.55 eV determined here is completely in line with the reported values. The decrease in work function after evaporation observed for chromium was also observed in the case of titanium. This, no doubt, has to do with the equilibration of the surface of the film with the constituents of the high vacuum system. This again points up the high sensitivity of work functions to the condition of the emitting surface.

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