FINAL REPORT
SINGLE CRYSTAL CLEAN WORK FUNCTIONS
AND THE BEHAVIOR OF VARIOUS ADSORBATES
ON METAL SURFACES

by

A. E. Bell, C. J. Bennette, R. W. Strayer and L. W. Swanson

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NASA Lewis Research Center
Cleveland, Ohio
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Direct Energy Conversion Division

Field Emission Corporation
McMinnville, Oregon
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Melrose Avenue at Linke Street
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ABSTRACT

Work functions (\(\Phi\)) and temperature coefficients (d\(\Phi\)/dT) were determined by the relative field emission method for various planes of Re, Nb and Ni and for single planes of W, Nb, Ni, Cu and Re by an absolute method. Activation energies of desorption of neutral Cs atoms were measured as a function of coverage from W/O, W/F and Re substrates. Terminal neutral Cs desorption promoted removal of F but not O from W. Cs is more strongly bound to the (0001) and (1012) planes of Re than to the (10\bar{1}4) plane.
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Cross section of electrostatic deflection probe tube.

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SUMMARY

Two methods were used for obtaining clean single plane values of work function. The first, field emission probe hole method, is a relative method and relies on assignment of a value to the average work function for the whole emitter. The second is an absolute method which depends on the fact that field emitted electrons originate at the Fermi level of the emitter and are only collected if the collector is biased to at least the value of the collector work function. Using the relative method and assuming that \( \phi_{av}(\text{Re}) = 4.88 \, \text{eV} \), \( \phi_{av}(\text{Nb}) = 3.99 \, \text{eV} \) and \( \phi_{av}(\text{Ni}) = 5.00 \, \text{eV} \) where \( \phi_{av} \) is the field emitter average work function, the following temperature coefficients (in units of \( 10^{-4} \text{eV/deg} \)) were measured: (0001) Re, \(-0.95 \pm 0.13\); (1010) Re, \(-1.13 \pm 0.66\); (10\( \bar{1} \)1) Re, \(-0.52 \pm 0.82\); (11\( \bar{2} \)0) Re, \(1.81 \pm 0.83\); (110) Nb, \(-0.98 \pm 0.43\); (100) Nb, \(-0.31 \pm 0.39\); (211) Nb, \(-0.31 \pm 0.27\); (111) Nb, \(1.64 \pm 0.23\); (111) Ni, \(-0.49 \pm 0.78\); (211) Ni, \(1.47 \pm 0.21\). Work functions were found to be (0001) Re, 6.49 eV; (10\( \bar{1} \)0) Re, 5.83 eV; (10\( \bar{1} \)1) Re, 5.69 eV; (11\( \bar{2} \)0) Re, 4.91 eV; (110) Nb, 4.95 eV; (211) Nb, 4.24 eV; (310) Nb, 4.27 eV; (111) Nb, 4.06 eV; (100) Nb, 3.87 eV; (111) Ni, 5.89 eV; and (211) Ni, 4.98 eV. Using the absolute work function method with macroscopic single crystals, the following work functions were obtained at 77°K: (110) W, 5.245 eV; (100) W, 4.609 eV; (100) Nb, 4.093 eV; (100) Ni, 5.491 eV; (100) Cu, 4.670 eV; (0001) Re, 5.285 eV. At 300°K, the following values were obtained: (110) W, 5.283 eV; (100) W, 4.612 eV; (100) Nb, 4.086 eV; (100) Ni, 5.463 eV; (100) Cu, 4.621 eV; (0001) Re, 5.295 eV. The disparities between the relative and
absolute methods for (110) W and (0001) Re are discussed in terms of spe-
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work function values obtained are satisfactorily explained in terms of Steiner
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Activation energies of desorption of Cs from the substrates W/O, W/F were determined as a function of Cs and O or F coverage. For the
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minal desorption energy of Cs from Re is $3.1 \pm 0.3 \text{ eV}$. 
WORK FUNCTION MEASUREMENTS OF VARIOUS SINGLE CRYSTAL FACES
OF RHENIUM, NIOBIUM, COPPER, AND TUNGSTEN

INTRODUCTION

For a number of years scientists have recognized the fact that the electron emission characteristics of a metal differ for different crystallographic orientations. Recently, refined techniques for obtaining high purity, well-defined single crystal surfaces have made it possible to explore the directional dependence of the work function for a number of materials. As a result, a considerable amount of experimental data has been generated by measuring contact potential differences and by analyzing various types of electronic emission.

It has become increasingly obvious that there can be significant differences in the values of work function for the same material and crystallographic direction depending upon the measuring technique used. In particular, for certain planes of some metals, work functions determined by field emission techniques are several tenths of a volt higher than the values determined other ways. For example, the field emission value of work function $\phi$ for the (110) plane of W is at least 0.6 eV higher than that obtained by other methods.\(^1\) A critical examination of the experimental techniques and methods of analyzing data should indicate possible reasons for these discrepancies.

In general, thermionic measurements involve a diode in which a single crystal cathode is heated and the current is monitored as a function
of temperature. The work function is obtained from the slope of a Richardson plot of log \( J/T^2 \) vs 1/T. This plot is based on the Richardson equation:

\[
J = A_R T^2 \exp \left(-\frac{\phi_R}{kT}\right)
\]  (1)

where the Richardson work function \( \phi_R \) is a constant independent of \( T \), \( A_R \) is the ideal Richardson constant equal to 120 amps/cm\(^2\)/°K, and \( k \) is Boltzmann's constant. A number of factors can cause deviations in the experimentally determined values of \( \phi_R \) and \( A_R \). These include space charge, Schottky effect, reflection, patch effects, geometry and other factors associated with the particular experimental arrangement. Also, the true work function of a practical surface is a function of temperature.

A modification of the thermionic diode that minimizes the effects of space charge, nonuniformity of electrodes, and geometrical influences is the Shelton retarding potential triode.\(^2\) The electron beam from a heated single crystal cathode passes through an aperture in the anode and enters a retarding field. The beam electrons are constrained by a strong magnetic field to move in tight spirals parallel to the magnetic field; thus, their transverse energy distribution is conserved. The cross sectional area of the collected beam is just that of the aperture. Since the aperture diameter is known, the current density at the collector can be determined from the magnitude of the collected current. By analyzing the collected current as a function of the retarding potential between the emitter and the collector, the temperature of the emitter and the saturation current density, the contact potential can be determined. In addition, the variation of work
function with temperature, $d\phi/dT$, can be measured by observing the change in contact potential with temperature. Knowing the temperature and the current density at a constant retarding potential, Richardson plots can be constructed from which the absolute value of the emitter work function can be obtained.

The field emission approach to measuring the dependence of $\phi$ upon crystallographic direction is similar to that used in field emission microscopy. A small probe hole in the anode allows collection of only those electrons emitted from a small portion of the needle point surface. If a sufficiently small aperture is used only electrons emitted from a single plane pass through the hole. Analysis of the $I(V)$ data of both the single plane and the total tip offers a method of determining the work function of that plane relative to the average work function for all planes.

Absolute values of work functions can also be ascertained using field emission probe methods by combining energy distribution measurements with $I(V)$ measurements. The analysis, based on the Sommerfeld free electron model, assumes a Fermi-Dirac electron energy distribution and neglects band structure effects. This method must be used with care, particularly for transition metals where significant deviations from the free electron model occur. This is particularly true of metals that possess narrow, nearly filled d bands in certain directions, where band structure effects can be significant.

The onset of field emission occurs with a well-defined, narrow spread of electron energy concentrated about the Fermi level. Therefore a field
emission electron source operated in a retarding potential mode is a very accurate tool for measuring absolute work functions of macroscopic single crystal collectors. Dyke originally recognized the significance of the technique for allowing absolute work function of the collector to be measured without requiring any knowledge of the work function of the emitter. Briefly, a retarding potential is applied between the emitter and the collector, and the collector current is measured as a function of the retarding potential. When the difference in potential between the emitter and collector is equal to the work function of the collector, there is a sharp increase in collected current. The experimental I(V) curve represents the integral of the energy distribution of the field emitted electrons.

Among the various techniques that have been described, the field emission retarding potential offers the most direct way of obtaining the absolute value of $\Phi$ for a macroscopic single crystal. The field emission probe technique offers the simplest method of obtaining relative work functions of a number of different planes from an atomically clean, nearly perfect surface. These two combined approaches offer a unique way of ascertaining absolute values of $\Phi$ for a large number of single faces of a particular metal. We have combined these two techniques in an attempt to measure $\Phi$ for various planes of several metals that are of interest for electrodes in thermionic energy converters.

This report includes a detailed discussion of these two experimental techniques used under the present contract effort for measuring the directional dependence of $\Phi$. The field emission probe method was used for
various planes of rhenium, niobium, and nickel, while the field emission retardation potential technique was used for the (0001) rhenium, (100) niobium, (100) nickel, (100) copper, (100) tungsten, and (110) tungsten planes. These results are summarized and compared with the best thermionic and contact potential values that could be found in the literature. Finally, an attempt is made to evaluate these results in terms of existing theories of clean work function metals.

**Description of Experimental Procedures**

Field emission microscopy has been used to measure the work functions of single crystal planes of Re, Nb, and Ni relative to the average work function of the polycrystalline specimen. By repeating these measurements at different temperatures, local variations in work function with temperature for the individual planes were evaluated.

The method involves measuring the emission characteristics of the entire tip and comparing this with the emission from a single plane. The working equation for field emission

$$\log \frac{I}{V^2} = m/V + \log A$$

has been programmed on a digital computer. The computer uses a least squares analysis of the I(V) data in the general linear form $y = m + b$, (where $y = \log \frac{I}{V^2}$ and $x = 1/V$) to obtain values of the slope $m$ and intercept $\log A$.

According to the Fowler-Nordheim equation for field emission, the
slope \( m \) is related to the work function \( \phi \) as follows:

\[
m = c \frac{\phi^3}{\beta}
\]

(3)

where \( c \) is a constant, and \( \beta \) is a geometrical factor relating the field at the tip to the applied voltage. If the average work function \( \phi_{av} \) is known, the relative work function of a single plane can be obtained from the slopes of the total and single plane \( I(V) \) data through the relationship:

\[
\frac{\phi_{rel}}{\phi_{av}} = \left( \frac{m_{rel}}{m_{av}} \right)^{2/3} \left( \frac{\beta_{rel}}{\beta_{av}} \right)^{2/3}
\]

(4)

where the subscripts refer to the emission characteristics averaged over the total tip area and over a single plane relative to the total. Similarly, if the work function of any single plane is known, the work function of any other plane relative to that of the known plane can be ascertained.

In the special case where the plane being probed is a high emission plane on axis \(^1\), \( \beta_{rel}/\beta_{av} = 1 \). In general the plane being probed is off axis. The variation in \( \beta \) (i.e., of local electric field at a given applied voltage) with angular separation from the emitter apex is one of the primary difficulties associated with using Eq. (3). The increased shielding of the tip by the emitter shank causes a monotonic decrease in \( \beta \) with increasing angle of deflection. Thermodynamically motivated local faceting of certain crystal faces also causes variations in \( \beta \). This faceting varies in magnitude with the temperature at which the tip was annealed prior to thermal quenching and is largest for the low index planes because of their lower surface energy.

The correction factor for the first of these problems has been deter-
mined experimentally in previous work here.\textsuperscript{1-8} The method involved measuring the relative variation in $m_{\text{rel}}$ for various \{310\} planes along the [100] zone line of a [310]-oriented W tip. By assuming that each (310) plane has the same value of $\theta_{\text{rel}}$, the correction factor for the relative variation of $\beta$ with reflection angle was obtained.

The effect of annealing temperature on the value of $\theta_{\text{rel}}$ is slight; however, an attempt was made to measure all planes of a given material after annealing at the same temperature. In this way the thermal end form should have been reasonably uniform for any one material.

In order to measure $\theta_{\text{rel}}$ at elevated temperatures, the more general TF (thermal field) formulation of the field emission equation must be used.\textsuperscript{9} This adds a correction term to $m_{\text{rel}}$ in Eq. (4) so that the working equation including corrections for temperature $T$ and angular deflection $\theta$ becomes:

$$\theta_{\text{rel}}(T) = \theta_{\text{av}}(T=0)[\frac{m_{\text{rel}}(T) + \delta}{m_{\text{av}}(T=0)}]^{2/3} \left[\frac{\beta(\theta)}{\beta(\theta=0)}\right]^{2/3}$$

where the temperature correction term

$$\delta = V(1 - \pi p \cot \pi p)/2.3$$

must be added to $m_{\text{rel}}$ obtained from computer analysis of the probe $I(V)$ data. Here

$$p = 8.82 \times 10^{-3}T\theta_{\text{rel}}^{1/2} t(y)/F$$

where $t(y)$ is a slowly varying tabulated function of $F$ and $\phi$, and $V$ is the mid-range value of voltage.\textsuperscript{9} A further correction for thermal expansion of the
heated emitter could be added. However, for the temperatures over which our measurements were made, this correction is negligible.

The (0001) Re measurements were obtained in the electrostatic deflection tube (Fig. 14) described in a later section of this report. The magnetic deflection probe tube (Fig. 1) used for all other measurements was based on a design by van Oostrom of the Phillips Laboratory. Briefly, the magnetic deflection tube is designed in such a way that electrons passing through the lens system are focussed near the center of the spherical collector F. The electrode system consists of an anode D, a focussing electrode E, a Faraday cage G. The latter electrode is operated near ground potential and acts as a shield for the hemispherical collector.

The tube, constructed of aluminosilicate glass, contained Mo electrodes and a hot-spun Mo collector cup (radius of curvature 15 mm) polished so that surface roughness was less than 1μ. The electrode apertures were 1, 2, and 4 mm, increasing in size toward the collector. A thin Willemite screen on the anode allowed pattern viewing.

Immersion of the tube into a cryostat of liquid nitrogen greatly increased vacuum stability, reduced tip contamination from the screen to a negligible amount during the emission of high total currents (up to 20 μA for Re), and extended the lower limit of temperature to 77°K.

The emitter assembly A consisted of a field emission tip of the desired material (Re, Ni, or Nb) spot welded to a 0.010 inch D tungsten filament. The tip was resistively heated by passing current through the support filament. The resistance changes could be accurately measured by
Figure 1. Cross section of magnetic deflection probe tube.

(A) emitter assembly;   (E) anode;  
(B) space for electromagnet;  (F) lens electrode;  
(C) cesium source platform;  (G) spherical collector;  
(D) oxygen source;  (H) Faraday cage;
sampling the potential changes across a small length of filament with 0.003 inch D wires attached to either side of the emitter. The temperature of the tip is determined from the known relationship between resistivity and temperature.

A small rotatable electromagnet B and internal concentrator C (Fig. 1) were used to deflect the beam in order to position the emission from the desired crystallographic plane onto the aperture of the anode. The internal concentrator could be tied electrically to the anode by allowing it to rest on a small Pt ring.

During the I(V) measurements with magnetic deflection, compensation for the changes of magnetic field with applied voltage were required in order to maintain a constant position of the desired crystal face on the aperture. To do this, work function measurements were taken along zone lines at positions where the collected current went through either a maximum or a minimum as a function of beam deflection. This allowed precise positioning of the desired crystal face on the aperture of the anode throughout the voltage range.

The ratio of the lens voltage \( V_L \) to the anode voltage \( V_A \) is a critical parameter and must be kept constant so that the electron trajectories through the lens remain constant over the voltage range. Best working conditions were determined to be those for which the ratio \( V_L/V_A = 0.10 \).

In order for the field emitted electrons to reach the collector, a bias voltage equal to or greater than the collector work function must be applied to the tip. Several values of bias voltage were tried in the range -6.0 V to
-22.5 V with little effect on the linearity of the I(V) characteristics. Most of the work was done with the tip biased at -9.2 V.

Fabrication of tips followed the usual electrolytic etching procedure.\textsuperscript{10} The etch solutions were as follows: Re (2N NaOH); Ni (HCl diluted with 60\% water); Nb (60\% H\textsubscript{2}SO\textsubscript{4} and 40\% HF). The oriented Re and Nb tips were made from zone melted stock. Two tip orientations were required for the Re measurements. For one tip, the (0001) plane was on axis; for the other, the tip was oriented such that an equatorial plane very near the (11\overline{2}0) was on axis. The Nb tips were oriented with the (310) plane on axis. With these orientations, the planes of interest were less than 44° off axis.

In general, field emitters are cleaned thermally by flashing at a temperature sufficiently high to cause dulling. The Nb and Re tips were successfully cleaned by this high temperature flash heating treatment. However, the Ni tips were considerably more difficult to clean. The procedure that seemed to work best with Ni was to heat at a lower temperature than that required for rapid dulling for several minutes (~1200°K). By going up slowly in temperature and reducing the time, clean tips could be obtained, but they were generally quite dull. Hydrogen was also introduced and the tip heated in a fairly high pressure of hydrogen. This latter technique was abandoned since it did not appreciably increase the chance of obtaining a clean tip. Altogether ten attempts were made to obtain clean Ni tips; only two of these were successful. Tips made from high purity, zone refined and oriented Ni stock could not be cleaned; tips made from high purity 0.002 inch D Ni wire were successfully cleaned. However, only [\text{111}] -oriented Ni tips could be
obtained in this manner.

The cleanliness of the surface can be determined from the appearance of the field emission pattern. The tip was deemed clean when the pattern was smooth and characteristic of the crystal structure of the metal (bcc for Nb, fcc for Ni, and hcp for Re). The patterns for Ni and Re were similar to those described in earlier work at this laboratory. The Nb tips quite unexpectedly showed a dark (310) plane. In most bcc metal crystals, the (310) plane is bright, indicating that the work function is low. For W, the (310) plane has the lowest work function. The fact that the (310) plane of Nb was dark suggested that there could have been an impurity in the bulk or that the vacuum was not good. Both possibilities were explored with negative results. The reproducibility of the pattern with several different tips also suggested that this high (310) plane could be a true characteristic of Nb.

The general experimental procedure was as follows:

1. The tip was thermally cleaned by flashing at a temperature sufficiently high to cause dulling. Subsequent flashing at slightly lower temperatures resulted in a clean surface without further dulling.

2. The magnet was positioned so that emission from the desired plane was intercepted by the anode probe hole.

3. The tube was immersed in liquid nitrogen and the tip was annealed by heating for a period of time at a particular temperature. The annealing time temperature varied with the metal being tested. For Re and Nb 1000°K for 300 sec was used for all except the (0001) Re measurement;
for the latter plane, 1745°K for 120 sec was used. Measurements were taken on a flashed Nb end form (∼2100°K flash). The Ni tip was annealed at 1500°K for 120 sec for the (111) measurement and at ∼700°K for 300 sec for the (211) measurement.

4. The beam was deflected and the I(V) characteristic at various temperatures was measured for the plane of interest. The total current was measured simultaneously with the probe current.

5. After each θ measurement, an I(V) check was made at 77°K in order to detect any changes in emission characteristic caused by contamination of the tip during the run.

6. The tube was pulled out of the dewar, the magnet repositioned for the next plane to be measured and steps 3 to 5 were repeated.

Results and Discussion

Single plane dθ/dT. The temperature dependence of the relative work function of several major directions of Re, Ni, and Nb are shown in Figs. 2, 3, and 4. The maximum tip temperature for these measurements was slightly below the threshold for field induced surface rearrangement due to atomic migration. The results show that the temperature coefficient of work function dθ/dT is reasonably constant over the range of temperatures covered. In addition, dθ/dT varies in both sign and magnitude with crystal direction.

The results (Figs. 2 - 4) are listed in Table I along with data obtained earlier for W and for Mo. It is interesting to note that dθ/dT is most
Figure 2. Plots of work function versus temperature for the (0001), (10\overline{1}0), (10\overline{1}1) and (1\overline{1}2\overline{0}) planes of Re.
Figure 3. Plots of work function versus temperature for the (111) and (211) planes of Ni.
Figure 4. Plots of work function versus temperature for the (110), (211), (111) and (100) planes of Nb.
negative for the densely packed high $\phi$ planes. This suggests that $d\phi/dT$ is closely related to the structure of the surface.

**TABLE I - TEMPERATURE DEPENDENCE $d\phi/dT$ FOR VARIOUS PLANES OF W, Mo, Nb, Ni, Re OBTAINED FROM FIELD EMISSION PROBE MEASUREMENTS AT VARIOUS TEMPERATURES. VALUES ARE GIVEN IN UNITS OF $10^{-4}$ eV/deg.**

<table>
<thead>
<tr>
<th>Metal</th>
<th>(110)</th>
<th>(100)</th>
<th>(211)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>-1.70</td>
<td>-1.09</td>
<td>-1.43</td>
<td>.35</td>
</tr>
<tr>
<td>Mo</td>
<td></td>
<td>-1.44</td>
<td>-0.40</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>-0.98±0.43</td>
<td>-0.31±0.39</td>
<td>0.31±0.27</td>
<td>1.64±0.23</td>
</tr>
</tbody>
</table>

**FCC**

<table>
<thead>
<tr>
<th>Metal</th>
<th>(111)</th>
<th>(211)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>-0.49±0.78</td>
<td>1.47±0.21</td>
</tr>
</tbody>
</table>

**HCP**

<table>
<thead>
<tr>
<th>Metal</th>
<th>(0001)</th>
<th>(10\overline{1}0)</th>
<th>(10\overline{1}1)</th>
<th>(11\overline{2}0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>-0.95±0.13</td>
<td>-1.13±0.66</td>
<td>-0.52±0.82</td>
<td>1.81±0.83</td>
</tr>
</tbody>
</table>
Blevis and Crowell\textsuperscript{14} advance a simple thermodynamic argument to show that the work function approaches a value independent of crystal orientation at the melting point. Bolshov\textsuperscript{15} has found that thermionic emission from pure Cu varies continuously as the temperature is raised through the melting point; his measurements provide support for the above viewpoint. Also, extrapolation of the temperature dependence of single-crystal face work functions of Cu (as determined from retarding potential data) and of W (determined from thermionic data, assuming the Richardson constant $A_R$ is $120 \text{ A/cm}^2/\text{K}$) in general approach a common value of work function for each metal at its melting point.\textsuperscript{14}

In Fig. 5, the data of Figs. 2, 3, and 4 are plotted (solid lines) and, using the calculated values of $d\phi/dT$, are extrapolated (dashed lines) to obtain work functions of single-crystal faces at the melting point for Re, Nb, and Ni; similar plots of W and Mo data obtained earlier in this laboratory\textsuperscript{1, 13} are shown in Fig. 6. These data also indicate a general trend towards a common work function at the melting point of a particular metal (with some exceptions: (0001) Re, (100) Nb, and (110) W), although the scatter in values at the melting point is considerably larger than in the results quoted in reference 14. The larger scatter is not surprising, because (1) the extrapolation is over a greater temperature range in the present case, and (2) the temperature coefficients $d\phi/dT$ measured here have fairly large uncertainties associated with them. The average values of work function at the melting point calculated from field emission data in this and earlier reports\textsuperscript{1, 13} are:
Figure 5. Extrapolations of the work function versus temperature curves up to the melting point of the metals for various planes of Re, Nb and Ni.
Figure 6. Extrapolation of the work function versus temperature curves up to the melting point of the metals for various planes of W and Mo.
Re 5.67 eV  
Nb 4.32  
Ni 5.52  
W 4.54  
Mo 4.32

The implicit assumption that $d\phi/dT$ is a constant over the temperature range from absolute zero to the melting point is not supported by theory; however, more accurate data are needed to specify $d\phi/dT$ with higher precision.

**Single Plane Relative $\phi$ of Clean Nb, Ni, Re.** The results of the measurements of the work function of four major planes of Re, five of Nb, and two of Ni are listed below in Table II. The values of $\phi$, calculated according to Eqs. (2) and (5), and plotted as a function of $T$ in Figs. 2-4, were analyzed by applying the linear least squares relationship to the following:

$$\phi = \phi_0 + (d\phi/dT)T$$  \hspace{1cm} (6)

where $\phi$ is a function of $T$ and $\phi_0$ is the value of $\phi$ at $T = 0$. The values of $\phi_{av}$ used in Eq. (4) were values of the average $\phi$ found in the literature.\(^{17,18,19}\)

The following values of $\phi_{av}$ were used: Re, $\phi_{av} = 4.88$ eV; Nb, $\phi_{av} = 3.99$ eV; Ni, $\phi_{av} = 5.00$ eV.
TABLE II - DIRECTIONAL DEPENDENCE OF $\phi$ FOR Re, Ni, and Nb ALONG WITH THE SURFACE ATOM DENSITY OF THE VARIOUS PLANES.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Plane</th>
<th>$\phi$(eV)</th>
<th>Atom density x $10^{-18}$ (atoms/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>(0001)</td>
<td>6.49±0.01</td>
<td>15.10</td>
</tr>
<tr>
<td>Re</td>
<td>(10\overline{1}0)</td>
<td>5.83±0.03</td>
<td>8.10</td>
</tr>
<tr>
<td>Re</td>
<td>(10\overline{1}1)</td>
<td>5.69±0.04</td>
<td>7.10</td>
</tr>
<tr>
<td>Re</td>
<td>(11\overline{2}0)</td>
<td>4.91±0.04</td>
<td>9.35</td>
</tr>
<tr>
<td>Nb</td>
<td>(110)</td>
<td>4.95±0.01</td>
<td>13.10</td>
</tr>
<tr>
<td>Nb</td>
<td>(211)</td>
<td>4.24±0.01</td>
<td>7.54</td>
</tr>
<tr>
<td>Nb</td>
<td>(310)</td>
<td>4.27±0.02</td>
<td>5.89</td>
</tr>
<tr>
<td>Nb</td>
<td>(111)</td>
<td>4.06±0.01</td>
<td>5.33</td>
</tr>
<tr>
<td>Nb</td>
<td>(100)</td>
<td>3.87±0.01</td>
<td>9.23</td>
</tr>
<tr>
<td>Ni</td>
<td>(111)</td>
<td>5.89±0.03</td>
<td>17.40</td>
</tr>
<tr>
<td>Ni</td>
<td>(211)</td>
<td>4.98±0.01</td>
<td>7.35</td>
</tr>
</tbody>
</table>

The Table II results show several interesting features. First, the variation in work functions is not directly proportional to the surface atom density. For both Nb and Re, the second most densely packed plane has the lowest work function of any major plane. Second, the (310) plane of Nb has a work function as high as that of the (211) plane. This result does not agree with measurements of other bcc crystals, W and Mo, for which the (310) plane exhibited the lowest work function of any plane. Finally, the field emission probe value for the (0001) Re work function is about a volt higher than that obtained by thermionic technique or by the $\phi$ measurements of a macro-
scopic (0001) Re crystal in the field emission retarding potential technique. The unduly high value of $\theta$ for (0001) Re is similar to the (110) W results obtained by the field emission probe method. A discussion of the reason for these high values measured by the field emission probe method is found in a later section of this report.

The (310) Nb results are not yet understood; however, they are consistent with what would be expected from the dark appearance of the (310) plane in the field emission pattern. The reproducibility of the results for three different tips suggests that these results are correct.

FIELD EMISSION RETARDING POTENTIAL TECHNIQUE

Henderson and Badgley first used the retarding potential method as a way of investigating field emitted electrons; they found that a voltage greater than 4.3 volts had to be applied to a Cu collector in order to collect a measurable portion of the field emitted electrons. Dyke employed the field emission retarding potential technique to determine the work functions of polycrystalline metal surfaces; recently, Holscher revived the technique to measure the work functions of freshly evaporated Au and Ni films under ultra-high vacuum conditions. In the present work we use the technique to obtain the work function of selected crystal faces of macroscopic single crystal metal targets.

Basis of the Technique

The potential energy diagram of Fig. 7 illustrates the essential fea-
Figure 7. Potential energy diagram for a field emission retarding potential analyzer. When the collector is biased such that only electrons from the Fermi level of the emitter can reach the collector, the battery voltage $V_c$ is equal to the collector work function $\phi_c$. 
tures of the field emission retarding potential method. A high electrostatic field applied to an emitter surface narrows the surface potential barrier, so that electrons occupying energy levels near the Fermi level can tunnel through the barrier. The emitted electrons are accelerated in the region between the emitter and the anode, but are then retarded in the region between the anode and the collector. If the collector is connected electrically to the emitter, the Fermi levels of the two metals are at the same level and the emitted electrons are stopped by a potential barrier at the collector surface equal to its work function $\phi_c$. To collect the field emitted electrons, a voltage $V_c$ with magnitude (with respect to the emitter) $V_c \geq \phi_c$ must be applied to the collector. Thus at $0^\circ$K the onset of current at the collector occurs when $V_c = \phi_c$, the collector work function.

The shape of the collector current-voltage curve $I_C(V_C)$ is determined primarily by energy distribution of the emitted electrons; for an emitter at $0^\circ$K the current density per unit total energy $J(\varepsilon)$ is (assuming the Sommerfeld free electron model for the electron distribution among the energy levels within the metal):\(^{21,1}\)

$$J(\varepsilon) = \frac{J_0}{d} e^{\varepsilon/d}$$

(7)

where $J_0$ is the total emitted current density at $0^\circ$K, $\varepsilon$ is the energy of an electron relative to the Fermi level ($\varepsilon = E - E_f$), and the value of $d$ is given approximately by\(^1\)

$$d = 9.76 \times 10^{-9} F/\phi_e^{1/2}(eV)$$

(8)
where $F$ is the value of the electric field in $V/cm$ applied to the emitter surface and $\phi_e$ is its work function in eV. The collected current is obtained by integrating Eq. (7) over the filled energy levels down to a level $\epsilon$ determined by the collector voltage ($\epsilon = E - E_f = \phi_c - V_c$):  

$$I_c = \frac{I_o}{d} \int_{\epsilon}^{0} e^{\epsilon/d} d\epsilon = I_o (1 - e^{\epsilon/d})$$

or

$$I_c = I_o \left[ 1 - e^{-\frac{(V_c-\phi_c)}{d}} \right] \quad (9)$$

where $I_o$ is the total collected current. Note that $I_c \to 0$ at $V_c=\phi_c$. The $I_c(V_c)$ curve corresponding to Eq. (9) is plotted as the solid curve in Fig. 8.

Experimental collector current-voltage curves differ from the theoretical curve discussed above due to several effects. At emitter temperatures above 0°K there is a deviation in $I_c$ from the ideal cut-off at $V_c=\phi_c$, because there are electrons emitted from energy levels above the Fermi level. The effect of temperature on the total energy distribution of field emitted electrons has been calculated theoretically\textsuperscript{1,21} and verified experimentally.\textsuperscript{1,22} Increasing temperature broadens the energy distribution and lowers its peak value (Fig. 1 of Reference 1). At low temperatures the deviation from the ideal cut-off is small and may be easily corrected for.

If the assumption of a free electron density of states within the emitter is not valid, there can be a modification of Eq. (9) due to band structure effects.\textsuperscript{1} Experimentally measured variations in electron energy distribution curves for the $<100>$ directions of W and Mo have been correlated with
Figure 8. Collector current $I_C$ as a function of collector voltage $V_C$ for the (110) W target. The solid curve is the theoretical curve for $0^\circ$K.
certain features of energy-surface shapes inferred from bulk electronic measurements.\textsuperscript{1,23} Changes in Eq. (9) due to band structure effects can be avoided by choosing an emission direction for which the corresponding energy distribution curve is "normal", i.e., exhibits the exponential behavior of Eq. (7).

The finite resolution of the energy analyzing system may modify the collector current-voltage curve. Young and Kuyatt\textsuperscript{24} have calculated the influence of energy analyzer transmission function upon field emission energy distributions, and have found in general that increasing energy analyzer width broadens the energy distribution and lowers its peak value in much the same manner as increasing temperature. Furthermore, they have found that the slope of the log of the energy distribution is changed by less than 1\% when the analyzer width is changed from 0 to 100 mV; in terms of the collector current-voltage curve, this means the energy analyzer width affects mainly the region of the cut-off, but not the upper portion of the $I_C(V_C)$ curve, which still may be used to determine $\phi_c$.

Other effects that can modify the collector current-voltage curve are those due to the properties of the collector itself, such as its perpendicularity to the electron beam, its surface roughness, its heterogeneity in work function, and its reflection coefficient. The loss in resolution $\Delta E$ due to an electron beam of energy $E$ striking a target at an angle $\Theta$ is given by\textsuperscript{25}

$$\Delta E = E \sin^2\Theta.$$  

(10)

For 1 eV electrons the change in resolution for an angle of 3 degrees is less
than 3 mV, and thus negligible. As pointed out by Holscher\textsuperscript{6}, the effect of irregularities in the equipotential lines near the collector, caused by collector surface roughness, can be minimized by reducing the potential drop in the region near the collector. According to Heil\textsuperscript{26}, the different potentials presented at the surface of a metal by the differently oriented crystal surfaces converge exponentially to the average potential as one moves away from the surface. Therefore, when the potential drop in the region of the collector is kept small, the measured work function for the collector will be an area average of the differing work functions on the collector surface. Madey and Yates\textsuperscript{27} have recently measured an effective electron reflection coefficient $R_s$ for the (100) and (110) surfaces of W. They obtained values for 1-$R_s$ of 0.98±0.01 for (100) W and 0.60±0.02 for (110) W over the 1 eV energy range of interest in this work. No data has been found on the reflection coefficient in 0 to 1 eV energy range for the other metals of interest here. We have assumed that the reflection coefficient is a constant over the 0 to 1 energy range; a constant reflection coefficient does not affect the shape of the collector current-voltage curve.

**Methods of Obtaining Work Function from the Experimental Data**

Determination of the collector work function from the cut-off voltage can yield erroneous values for the reasons mentioned above; thus other methods of analyzing $I_C(V_C)$ data to yield $\phi_c$ are necessary. One technique is to fit graphically a logarithmic curve to the upper portion of the $I_C(V_C)$ curve.
and to extrapolate to $I_C = 0$. A second technique is to measure $V_C$ at which $I_C = 1/2 I_0$ (call it $V_{1/2}$); from Eq. (9),

$$ \phi_C = V_{1/2} - d(\ln 2). \tag{11} $$

A third technique involves rearranging Eq. (9) in the following form:

$$ \ln(I_O - I_C)/I_0 = (\phi_C - V_C)/d. \tag{12} $$

A plot of $\ln(I_O - I_C)/I_0$ as a function of $V_C$ is a straight line, the intercept of which is equal to the collector work function $\phi_C$. Since this method lends itself to least squares analysis, and is thus the most accurate, work functions obtained from Eq. (12) are quoted in the results listed below. Work functions obtained by the first two methods differed by less than 0.015 eV, on the average, from those obtained from Eq. (12).

**Description of Experimental Technique**

**Experimental Tube.** The design of the experimental tube used in the work function determinations by the retarding potential method is shown in Fig. 9. The electron gun portion of the tube is essentially the same as a field emission electron gun developed for LEED applications, and found to be suitable for retarding potential measurements. The emission source is a [111]-oriented W field emitter, which has a normal electron energy distribution along the emission axis. The anode voltage provides the high field necessary to obtain electron emission from the field emitter. Two
einzel lenses (6 electrodes) focus the divergent beam from the emitter into a nearly parallel beam at the collector. The Cu mesh voltage reduces the beam voltage to a few volts above the collector voltage. The Cu mesh collects the portion of beam current not retained by the collector, and establishes parallel equipotential lines in front of the collector. The target is cleaned by electron bombardment from a circular W filament concentric with the target surface. The target is replaceable, although a change in target requires a re-evacuation. The field emitter and first aperture are also replaceable. The diameter of the electron beam at the target is approximately 1 mm.

The targets were made from single crystal Marz grade rods. To obtain a particular target, the corresponding rod was first checked for orientation by means of its Laue backscattered X-ray pattern. The target was than machined into shape and its front surface electrolytically etched to remove work damage. A Laue pattern of the final target surface was taken to determine final orientation and to check for evidence of more than one crystal. The surface was next photographed at 300 x magnification. The target was then installed in the tube.

Procedure - The tube was evacuated on a liquid nitrogen trapped mercury diffusion system that was baked at 400°C. After outgassing the target and nearby elements by electron bombardment and obtaining a vacuum in the $10^{-10}$ torr range, the tube was sealed off for the first target, (110) W. However, it was found difficult to keep a good vacuum in the tube after many
heatings of the target. Therefore, for the remaining targets, the tube was operated on the vacuum system.

After ultra-high vacuum was attained, the emitter tip was flashed to 1900°K to obtain a reasonably clean surface and to reduce noise in the electron beam. Optimum focussing of the electron beam onto the target was achieved by maximizing the slope of the $I_c(V_c)$ curve in the low collector current region. The resolution of the tube could then be determined by plotting $I_c(V_c)$ data in the form $\Delta I_c/\Delta V_c$ versus $V_c$ (that is, in the form of an energy distribution plot) and determining the steepness of the leading edge of the resulting curve (Fig. 10). The difference in energy between the 10 and 90% points on the leading edge of the energy distribution curve has been related to the energy analyzer width (that is, the resolution of the experimental tube) by calculations of Young and Kuyatt. For an emitter at 77°K and from the data in Fig. 10, the best resolution of this particular experimental tube is 0.058 eV. Typical gun voltages to achieve optimum focussing were: anode, 1000 V; first einzel lens, 50 V; second einzel lens, 40 V; Cu mesh, 10 V.

In order to produce a clean target surface and to limit heating of nearby elements in the tube, the target was flash heated by electron bombardment. Targets were bombarded for a few seconds to reach temperatures as follows: 2100°K for Nb, Re and W; 1400°K for Ni; and 1100°K for Cu. Because of the possibility that the Ni and Cu surfaces may still have had some O on them at the indicated temperatures, they were first heated in a H$_2$ atmosphere at a pressure $>10^{-6}$ torr, and then heated in vacuum. The
Figure 10. Energy distribution of the collected electrons. The energy difference of 58 meV between 10 and 90% peak height values yields a value of 58 meV for the resolution of the experimental tube.
cycle was repeated until no change in work function resulted.

The emission current \( I_e \) at constant anode voltage \( V_a \) was checked before and after each target heating. An unchanged emission current indicated that no contamination had reached the emitter tip. This implies that negligible contamination was released by the target during flashing, and that the target was essentially clean.

During measurements the general experimental procedure was as follows:

1. The emitter was flashed to about \( 1900^\circ \text{K} \), after which the anode voltage was adjusted to obtain \( 0.5 \, \mu\text{A} \) emission current. During work function measurements the emitter temperature was \( 77^\circ \text{K} \).

2. The target was heated by electron bombardment for a few seconds to an appropriate temperature (listed above). Contamination was checked by noting any change in emission current.

3. If the contamination check was satisfactory, the collector current was plotted as a function of collector voltage \( V_c \) on an X-Y plotter. Both emitted current and collected current were measured by Keithley electrometers operated in the feedback or "fast" mode; thus the voltage drop across each meter was less than \( 1 \, \text{mV} \). The collector voltage was set by a Keithley 241 voltage supply, which has an accuracy of \( \pm 0.01\% \) or \( \pm 5 \, \text{mV} \).

4. Steps (2) and (3) were repeated ten to twelve times with the target at room temperature and at liquid nitrogen temperature for each target.

5. The resulting \( I_c(V_c) \) data were analyzed according to Eq. (12) by a high-speed digital computer, using a least squares analysis fit to a straight
Results and Discussion

Surface Conditions - The micrographs taken of the target surfaces are shown in Fig. 11. The (0001) Re micrograph shows several crystal boundaries intersecting the surface. A Laue pattern of the surface indicated that the surface is made up of several crystals whose surface normals lie within 2 degrees of the [0001] direction. As the whole Re sample from which the target was produced was similar, the surface that we obtained was the best possible, under the circumstances.

All of the target surfaces had some degree of surface structure, as revealed by the micrographs. The Laue patterns of the targets were sharp, however, indicating that the targets were single-crystal (except Re). The deviations of the surface normals from the desired directions, as obtained from the Laue patterns, are given in Table III. None of the deviations are large enough to cause a significant change in work function.

<table>
<thead>
<tr>
<th>Material</th>
<th>Angle between axis and crystal face normal</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110) W</td>
<td>2.9±0.4°</td>
</tr>
<tr>
<td>(100) W</td>
<td>2.3±0.4°</td>
</tr>
<tr>
<td>(100) Nb</td>
<td>0.5±0.4°</td>
</tr>
<tr>
<td>(100) Ni</td>
<td>0.7±0.3°</td>
</tr>
<tr>
<td>(100) Cu</td>
<td>1.0±0.3°</td>
</tr>
<tr>
<td>(0001) Re (average)</td>
<td>0.6±0.3°</td>
</tr>
</tbody>
</table>
Figure 11. Micrographs of target surfaces.
Work function values - The work function values obtained by the field emission retarding potential technique are listed in Table IV. The uncertainties listed in the table show the spread in the values obtained. The overall accuracy of the experimental technique is estimated to lie between ± 0.01 and ± 0.02 eV. Comparison of these results with other experimental results is given in the following section. In this section we estimate the reliability of present measurements.

The main sources of possible error in these measurements are changes in work function due to patch fields associated with surface roughness or to surface contamination. Since the measured work function is an area average of any differing work functions of the surface, the error in work function is proportional to the fraction of surface area occupied by surface defects. For all targets except Re the fraction of surface area associated with surface defects is small; thus the corresponding error in work function is small. For Re, a high estimate of the fractional area taken up by crystal boundaries is 0.2; assuming that the work function of the crystal boundaries is 4.88 eV, the average work function for Re, the remaining area (the 0001 surface) then has a work function of 5.38 eV, less than 0.1 eV higher than the measured work function for (0001) Re.

Concerning the possibility of work function change due to contamination, the only target whose cleanliness is in doubt is (100) Cu. The (100) Cu surface may not really have been clean despite the repeated heatings in H₂ atmosphere and in vacuum. In an earlier use of this procedure the Cu was heated hot enough to melt. The resulting work function was 4.90 eV as com-
pared to 4.62 eV. The difference may be due to a cleaner surface obtained by partial melting of the target. More data is needed to confirm the present measurement.

### Table IV - Work Function Values Obtained by Field Emission Retarding Potential Technique

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°K)</th>
<th>( \varnothing ) eV</th>
<th>Deviation eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110) W</td>
<td>77</td>
<td>5.245</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>5.283</td>
<td>0.016</td>
</tr>
<tr>
<td>(100) W</td>
<td>77</td>
<td>4.609</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>4.612</td>
<td>0.005</td>
</tr>
<tr>
<td>(100) Nb</td>
<td>77</td>
<td>4.093</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>4.086</td>
<td>0.009</td>
</tr>
<tr>
<td>(100) Ni</td>
<td>77</td>
<td>5.491</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>301</td>
<td>5.463</td>
<td>0.020</td>
</tr>
<tr>
<td>(100) Cu</td>
<td>77</td>
<td>4.670</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>4.621</td>
<td>0.010</td>
</tr>
<tr>
<td>(0001) Re</td>
<td>77</td>
<td>5.285</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>(multicrystal)</td>
<td>5.295</td>
<td>0.011</td>
</tr>
</tbody>
</table>

### Comparison of Results with Theory and Other Experimental Data

**Other Experimental Results**

Table V summarizes our measurements by the field emission probe and field emission retarding potential (f.e.r.p.) techniques and compares them with results from corresponding thermionic techniques. The agree-
ment is good on all planes of W except for (110) W by the field emission probe technique. Agreement is fair for most planes of Mo and Nb. The (100) Cu work function by the f.e.r.p. technique is somewhat lower than the corresponding thermionic measurement. For Re, the field emission probe work functions are consistently higher, while f.e.r.p. work function measurement is lower. The largest differences are in the work function values for the high work function planes of W and Re. These differences will be discussed in the section comparing thermionic and field emission techniques.

**Theoretical and Semi-empirical Correlations**

The most adequate theory for predicting the directional dependence of $\phi$ for clean metals must account for the experimental fact that suggests that $\phi$ is strongly related to the geometrical or the electronic structure of the surface. Table II shows that $\phi$ is proportional to the atom density on the surface except for the (100) direction of Nb and the (1120) direction of Re. A theory that can predict these results would have merit enough to be worth careful consideration.

There are several theories that have evolved over the past few decades. Smoluchowski,$^{29}$ following the work of Wigner and Bardeen,$^{30,31}$ separated $\phi$ into a sum of a volume contribution and a contribution to the potential due to a surface double layer. The origin of this double layer comes from the idea of a redistribution of the electron cloud on the surface. This causes a spreading out of the charge over the surface and also
tends to smooth out the negative charge surface so that surfaces of equal
charge density are more nearly plane. From these considerations, Smolu-
chowski calculated differences in work function for the various faces of W.

A recent semi-empirical formulation by Steiner and Gyftopoulos makes use of the concept of electronegativity to derive an equation by which quantitative values of $\phi$ may be calculated with a minimum of assumptions. In this work, $\phi$ is defined in terms of the amount of work required to remove an electron from a valence orbital of a surface atom without altering the energy state of the atoms. This reduces the problem of calculating the work function to that of computing the energy per valence electron in a surface atom. By equating $\phi$ with the neutral orbital electronegativity, the following expression for $\phi$ is derived:

$$\phi = 0.98 \frac{v_s + 1}{r_m} + 1.57 \text{ (eV)} \quad (13)$$

where $v_s$ is the number of bonding electrons per surface atom, and $r_m$, the effective size of these atoms in angstroms, is assumed to be equal to the atomic radius.

In order to use Eq. (13) for calculating $\phi$, Steiner and Gyftopoulos derive the surface valence $v_s$ in terms of the metallic valence $v_m$ and the fractional bond numbers of atoms in the bulk. A brief outline of the method is presented in the following paragraphs.

The number of bonding electrons per atom in the bulk of a metal is defined as the metallic valence $v_m$. The average number of bonding electrons shared by two interacting atoms separated by a distance $R$ is $2n$, where
n is the fractional bond number. According to Pauling, the fractional bond numbers \( n_a \) and \( n_b \) associated with the interatomic separations \( R_a \) and \( R_b \) is given by:

\[
R_b - R_a = 0.26 \ln \left( \frac{n_a}{n_b} \right)
\]  

(14)

For bcc and hcp crystal structure, fractional bond numbers between atoms further distant than next nearest neighbors are negligible. For fcc fractional bond numbers between atoms further distant than nearest neighbors are negligible. The metallic valence and fractional bond numbers for the various crystal structures are given by:

\[
v_m = 8n_a + 6n_b \quad \text{for bcc}
\]

\[
v_m = 6n_a + 6n_b \quad \text{for hcp}
\]

\[
v_m = 12n_a \quad \text{for fcc}
\]

where \( n_a \) and \( n_b \) are the fractional bond numbers for nearest and next nearest neighbors, respectively. Tabulated values of metallic valence and interatomic distances can be used in Eqs. (12) and (24) to compute the fractional bond numbers \( n_a \) and \( n_b \). If it is assumed that the fractional bond numbers of atoms on the surface are identical to those of atoms in the bulk, then the surface valence is given by:

\[
v_s = N_a n_a + N_b n_b \quad \text{for bcc and hcp}
\]

\[
v_s = N_a n_a \quad \text{for fcc}
\]

(16)

where \( N_a \) and \( N_b \) are the number of nearest and next nearest neighbors of
surface atoms respectively. The numbers $N_a$ and $N_b$ are fixed by the crystallographic orientation of the surface.

The semi-empirical approach outlined above allows for computations of $\varnothing$ to be made based on known properties of metals. Following this procedure work function values for the metals and orientations of this work were computed. The agreement was sufficiently encouraging that values were calculated for a number of other metals and crystal directions for which experimental data was available from the literature. The results are shown in Table V. In order to correlate the Table V results with the discussion of the relationship between the value of the work function measured and the method of obtaining that measurement, the experimental values of $\varnothing$ are separated according to the measuring technique that was used. Numbers in parentheses are references to the literature.

The remarkably good agreement between Eq. (13) and experiment for the substrates listed in Table V reemphasizes the observation that the electronic structure of the surface is significant in predicting the clean work function of the surface. The most significant factors in determining the work function of a metal surface according to this theory are the number of ligands possessed by an atom on the surface, the interatomic distances between that atom and its ligands, and the metallic valence. The high work function planes are those for which the number of ligands and the metallic valence are large, and the interatomic distances are small.
TABLE V - COMPARISONS OF $\phi$ OBTAINED BY THERMIONIC, THERMIONIC RETARDING POTENTIAL, FIELD EMISSION RETARDING POTENTIAL, AND THE CALCULATED VALUES ACCORDING TO THE THEORY OF STEINER AND GYFTOPOULOS.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\phi$ (eV) Thermionic</th>
<th>$\phi$ (eV) Thermionic Retarding Potential</th>
<th>$\phi$ (eV) Field Emission Probe</th>
<th>$\phi$ (eV) Field Emission Retarding Potential</th>
<th>$\phi$ (eV) Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>W (110)</td>
<td>5.35 ± 0.05 (36)</td>
<td></td>
<td>5.9 ± 1 (1)</td>
<td>5.25 ± 0.01</td>
<td>5.50</td>
</tr>
<tr>
<td>W (100)</td>
<td>4.60 ± 0.05 (36)</td>
<td></td>
<td>4.70 ± 0.05 (1)</td>
<td>4.61 ± 0.01</td>
<td>4.66</td>
</tr>
<tr>
<td>W (112)</td>
<td>4.80 ± 0.05 (36)</td>
<td></td>
<td>4.9 ± 1 (1)</td>
<td>4.94</td>
<td></td>
</tr>
<tr>
<td>W (111)</td>
<td>4.40 ± 0.02 (36)</td>
<td></td>
<td>4.45 ± 0.03 (1)</td>
<td>4.47</td>
<td>4.47</td>
</tr>
<tr>
<td>W (116)</td>
<td>4.32 ± 0.02 (36)</td>
<td></td>
<td>4.32 ± 0.04 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W (130)</td>
<td></td>
<td></td>
<td>4.25 ± 0.05 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo (110)</td>
<td>5.10 ± 0.05 (37)</td>
<td></td>
<td>4.8 ± 0.10 (13)</td>
<td>5.23</td>
<td></td>
</tr>
<tr>
<td>Mo (100)</td>
<td>4.90 ± 0.07 (38)</td>
<td></td>
<td>4.35 ± 0.02 (13)</td>
<td>4.44</td>
<td></td>
</tr>
<tr>
<td>Mo (112)</td>
<td>4.35 ± 0.07 (39)</td>
<td></td>
<td>4.51 ± 0.07 (13)</td>
<td>4.71</td>
<td></td>
</tr>
<tr>
<td>Mo (111)</td>
<td>4.53 ± 0.10 (39)</td>
<td></td>
<td>4.15 ± 0.10 (13)</td>
<td>4.27</td>
<td></td>
</tr>
<tr>
<td>Mo (116)</td>
<td>4.15 ± 0.05 (37)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta (110)</td>
<td>4.80 ± 0.02 (36)</td>
<td></td>
<td>4.35 (2)</td>
<td>4.75</td>
<td>4.08</td>
</tr>
<tr>
<td>Ta (100)</td>
<td>4.15 ± 0.02 (36)</td>
<td></td>
<td></td>
<td></td>
<td>4.31</td>
</tr>
<tr>
<td>Ta (112)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.94</td>
</tr>
<tr>
<td>Ta (111)</td>
<td>4.00 ± 0.02 (36)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substrate</td>
<td>$\phi$ (eV) Thermionic</td>
<td>$\phi$ (eV) Thermionic Retarding Potential</td>
<td>$\phi$ (eV) Field Emission Probe</td>
<td>$\phi$ (eV) Field Emission Retarding Potential</td>
<td>$\phi$ (eV) Calculated</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------------------</td>
<td>------------------------------------------</td>
<td>---------------------------------</td>
<td>-----------------------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Nb (110)</td>
<td>4.80±0.05 (40)</td>
<td></td>
<td>4.95±0.01</td>
<td>4.09±0.01</td>
<td>4.75</td>
</tr>
<tr>
<td>Nb (100)</td>
<td>3.95±0.03 (40)</td>
<td></td>
<td>3.87±0.01</td>
<td></td>
<td>4.08</td>
</tr>
<tr>
<td>Nb (112)</td>
<td>3.88±0.03 (40)</td>
<td></td>
<td>4.26±0.01</td>
<td></td>
<td>4.31</td>
</tr>
<tr>
<td>Nb (111)</td>
<td>3.70±0.03 (40)</td>
<td></td>
<td>4.05±0.01</td>
<td></td>
<td>3.94</td>
</tr>
<tr>
<td>Ni (111)</td>
<td></td>
<td></td>
<td>5.89±0.03</td>
<td></td>
<td>5.56</td>
</tr>
<tr>
<td>Ni (100)</td>
<td></td>
<td></td>
<td>4.98±0.01</td>
<td></td>
<td>5.20</td>
</tr>
<tr>
<td>Ni (112)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu (100)</td>
<td>4.9 (14)</td>
<td></td>
<td>4.67±0.02</td>
<td></td>
<td>4.99</td>
</tr>
<tr>
<td>Re (0001)</td>
<td>5.59±0.05 (18)</td>
<td>5.57 (18)</td>
<td>6.49±0.01</td>
<td>5.29±0.01 (multicrystal)</td>
<td>5.53</td>
</tr>
<tr>
<td>Re (1010)</td>
<td>5.2 ± 1 (18)</td>
<td></td>
<td>5.83±0.03</td>
<td></td>
<td>5.20</td>
</tr>
<tr>
<td>Re (1120)</td>
<td>5.37±0.03 (18)</td>
<td>5.12±0.20 (18)</td>
<td>4.91±0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re (10\bar{1}1)</td>
<td>5.69±0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
EVALUATION OF THERMIONIC AND FIELD EMISSION TECHNIQUES FOR MEASURING CLEAN METAL WORK FUNCTIONS

Within the past few years there has been considerable interest in measuring the true values of $\phi$ for single planes of clean metal surfaces with great accuracy. As a result of a careful literature search the measured values for a number of major planes of some of the transition metals are given in Table V. A cursory comparison of the values obtained by the different techniques shows that $\phi$ is essentially independent of the measuring technique with the notable exception of W (110) and all planes of Re. For these latter planes, field emission measurements are as much as 1.0 eV higher than either thermionic or retarding potential measurements.

It is interesting to note that two metals, Ta and Nb, with identical lattice parameters and similar electronic structures exhibit no anomalously high field emission $\phi$ for any plane. However, for W and Mo, two metals that also have identical lattice parameters but slightly different electronic structure, the field emission measurements give anomalously high (110) values of $\phi$ for W but not for Mo. A theory that will explain the 0.6 eV difference for the $\phi$ values measured by various methods for the (110) plane of W must also account for the good agreement with the (110) plane of Mo for all measuring methods. It must also explain why the (110) plane of W is the only major plane of W for which any discrepancy exists.

In attempting to understand these discrepancies, work function must
be defined in a generalized form that will fit all types of emission procedures. The best definition seems to be that $\phi$ is the maximum potential energy of an electron at the surface of an emitter, that is, $\phi$ is equal to the difference between the Fermi energy and the surface potential energy.

In a recent theoretical work, Itskovich extended the original Fowler and Nordheim theory of field emission to include the effects due to the complex electron dispersion within the metal. For these calculations, the electron wave functions outside the metal are written as products of plane waves in the $x$ and $y$ directions multiplied by functions of $z$. The wave functions inside the metal are superpositions of Bloch waves. The results of the calculation are that the principal contribution to field emission comes from electrons whose energy in the $z$ direction is a maximum. The principal difference between the equations for field emission current derived by Itskovich in which electrons obey a dispersion law, and the original Fowler-Nordheim model which is a special case of free electrons, consists in replacing $\phi$ by $\phi_{\text{eff}}$. The condition for $\phi = \phi_{\text{eff}}$ is when the Fermi surface surrounds the origin in $k$ space, particularly in the free electron model. Electrons that are emitted below the Fermi level or outside the conduction band reach a maximum energy in the $z$ direction that does not correspond to the maximum in the total energy, therefore $\phi_{\text{eff}} > \phi$.

The only value that can be determined from field emission measurements is $\phi_{\text{eff}}$. When $\phi_{\text{eff}} = \phi$, the Fermi surface is intersected by the $z$ direction of momentum, and when $\phi_{\text{eff}} > \phi$, it does not. If $\phi = \phi_{\text{eff}}$ for all directions, as is the case of Ta, Nb, and Mo, the conclusion is that the Fermi surface is intersected by all straight lines passing through the coordinate ori-
gin. The shape of the Fermi surface can be complex as in the case of Fig. 12a (reproduced from reference 40) and yet still enclose the origin. If $\theta_{\text{eff}} > \theta$ for only one or two directions and $\theta_{\text{eff}} = \theta$ for all other directions, the Fermi surface has a form similar to that shown in Fig. 12b (as in the case of Ni where the open directions correspond to the [111] necks). If $\theta_{\text{eff}} = \theta$ for many directions and $\theta_{\text{eff}} > \theta$ for the remaining ones, the Fermi surface consists of small pockets such as in Fig. 12c.

The original theory of field emission from metals was based on the free electron model. The anisotropy resulting from field emission data could be due to the differences between $\theta_{\text{eff}}$ and $\theta$ depending upon the form of the Fermi surface. Although the detailed Fermi surfaces for all of the metals listed in Table V are not well known, it is interesting to speculate that the large discrepancies between the values of $\theta$ measured by thermionic and by field emission techniques could be accounted for if these shapes were known. Recent work on the band structure and Fermi surface of Re$^{42}$ show that there is an open structure along the $<0001>$ direction, in which case $\theta_{\text{eff}} > \theta$. This may account for the unusually high value obtained by field emission methods. For W, the Fermi surface is very similar to that of Mo$^{43,44}$ except that in the $<110>$ direction, there are some "hole" pockets that are very small in W and large in Mo. However, the complete enclosure of the k-space origin by an electron surface rules out an explanation based solely on Itskovich's model.

Thermionic experiments also measure an effective thermionic work function.$^{45}$ The arguments are similar to those given above for field emis-
Figure 12. Various forms of Fermi energy surfaces.
sion except that now the energy surfaces are not the same as the ionic surface. The equal energy surfaces are defined such that the projection of the energy surface on the x-y plane in momentum space has a common point with the circle

\[ \frac{P_x^2 + P_y^2}{2m_0} \leq E + \frac{e^{3/2}F^{1/2}}{2} \]

Obviously the minimum energy of electrons escaping from the metal is the condition \( E_{\text{min}} \geq -e^{3/2}F^{1/2} \). For free electrons \( E_{\text{min}} = -e^{3/2}F^{1/2} \) and \( P_z \) intersects the energy surface \( E = -e^{3/2}F^{1/2} \). This is the only case for which \( \phi_{\text{eff}} = \phi \). For other cases \( \phi_{\text{eff}} > \phi \).

From the above discussion, it is obvious that only for free-electron type surfaces will \( \phi_{\text{eff}} = \phi \) independent of the technique of measuring \( \phi \). For field emission the critical parameter is the shape of the Fermi surface, and for thermionic emission, it is the shape of the vacuum level energy surface. However, the latter surface is generally much more highly developed, therefore there is a much greater probability that \( \phi_{\text{eff}} = \phi \) for thermionic emission than for field emission. Consequently the probability that

\[ \phi_{\text{eff}}(\text{F.E.}) \geq \phi_{\text{eff}}(\text{Thermionic}) \]

is much greater than the reverse. The experimental data shown in Table V substantiates this conclusion.

Other possible explanations of the discrepancies between field emission and thermionic emission measured work functions involve (1) surface band structure, \(^{45}\) (2) static field penetration and atomic polarization, \(^{46, 47}\)
differences in thermal disorder.

J. R. Smith\textsuperscript{45} points out that surface band structure may be very different from the bulk band structure and thus could account for the differences in work function measurements whereas the latter does not. However, the dependence of surface band structure upon crystallographic direction has not been evaluated yet and thus there are no details concerning how it may affect work functions of different planes.

The high electric fields required for field emission could affect the work function measurements.\textsuperscript{46,47} Tsong and Müller\textsuperscript{46} calculate an appreciable increase in work function for fields required for field ionization (4 to 5 V/Å). However, Kaplitt,\textsuperscript{48} following the formulation by Smoluchowski, has calculated the differences in work function for the principal planes of tungsten due to fields required for field emission (0.3 to 0.4 V/Å) and finds negligible differences for (110) W. Also, his calculations indicate that a high-field effect should be greater for a low work function plane (111 W) than for a high work function plane (110 W).

Thermal disorder and other surface defects can affect the value of work function as measured by the different techniques. Surface disorder can be essentially eliminated on the microscopic planes of a field emission tip; this probably is not possible on macroscopic planes. However, it is difficult to account for the disagreement on the (110) plane of W and the good agreement on the (110) plane of Mo by this explanation; both metals are refractory metals with nearly identical crystal structures.

The conclusions drawn from these considerations are the following:
(1) Retarding potential methods of determining work function are best for macroscopic surfaces. Surface defects are area-averaged rather than weighted towards low work function values, and thus will not change the work function measurement appreciably if their concentration is small.

(2) The field emission retarding potential technique has two advantages over the thermionic retarding potential technique: (a) a magnetic field is not required, and (b) the temperature of the emission source need not be measured or calculated accurately.

(3) The emission methods yield work function values in good agreement with each other and with the retarding potential methods for low work function planes. At present, no explanation seems adequate in accounting for the differences in work function measurements for the high work function planes of tungsten and rhenium.
ACTIVATION ENERGIES OF DESORPTION AND WORK FUNCTIONS OF CESIUM ON OXYGENATED TUNGSTEN, FLUORINATED TUNGSTEN, AND RHENIUM

In the study of low work function adsorbates, the favorable properties of the alkali and alkaline earth metals have long been recognized. For Cs adsorbed on W, work functions as low as 1.5 eV have been obtained and even lower values obtained when Cs was deposited upon chemisorbed layers of O and F. In addition, an increase in binding energy of Cs to the substrate - at least at low Cs coverages - occurs because of the presence of underlying O and F. In view of the very low work functions attainable in these coadsorbate systems, it is of interest to examine how the binding energy of Cs on W/F and W/O substrates varies with amount of adsorbed Cs and preadsorbed O or F. Included below is a table of a few of the pertinent physical properties of oxygen and fluorine:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Ionization potential V</th>
<th>Atomic radius Å</th>
<th>Electronegativity Pauling scale</th>
<th>Electron affinity eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>13.6</td>
<td>0.60</td>
<td>3.5</td>
<td>1.46</td>
</tr>
<tr>
<td>F₂</td>
<td>17.3</td>
<td>0.50</td>
<td>4.0</td>
<td>3.45</td>
</tr>
</tbody>
</table>

An earlier field emission study of the Cs/F/W system by Wolf\textsuperscript{49} showed remarkable similarities to the Cs/O/W system. For example both systems
have previously been observed to yield a work function as low as $\sim 1$ eV.

**Methods of Obtaining Activation Energies of Desorption of**

**Cesium from Fluorinated Tungsten and from Oxygenated Tungsten**

Most of the measurements in this section were carried out using field emission techniques with a 110 oriented emitter. Fig. 13 is a cross section of the field emission tube used in this work to obtain the average adsorption and desorption data. The tube was baked at 450°K prior to the Cs/O/W work and to 250°K prior to the Cs/F/W work; in the latter case, bakeout temperatures were restricted to 250°K in order to prevent diffusion of CsF from the CsF bucket source throughout the tube space. The vacuum processing included outgassing of various electrodes, careful outgassing of the CsF and O source. The O source was prepared by heating the finely granulated CuO source at dull red heat for several hours in $\sim 2$ cm of O$_2$; after processing, the tubes were sealed off under vacuum at a residual pressure of $< 10^{-8}$ torr. Operation of a Mo getter ensured a vacuum of $< 10^{-12}$ torr when the tube was operated fully immersed in LN$_2$. The tubes contain Cs break seal ampoules which were used as a reservoir of Cs for the Pt platform source. Cs was driven from the reservoir into the glass nozzle by heating a nichrome spiral around the reservoir. A Pt spiral around the nozzle was then heated to evaporate the Cs onto the LN$_2$ cooled platform source from which radial beams of Cs atoms could be projected to the emitter by heating the platform. If necessary, reproducible doses of any size
Figure 13. Cross section of field emission tube used to determine activation energies of Cs desorption from W/O and W/F substrates. For the F work, the Cu oxide source was replaced by a CsF source.
could be directed at the emitter merely by heating at fixed currents for controlled periods - usually 30 seconds - of time.

Before beginning desorption energy measurements, it was necessary to ensure that the emitter cap and shank were fully equilibrated with one another with respect to adsorbed Cs. The initial dose of Cs impinges nearly perpendicular to the emitter axis. When the emitter is then heated to a temperature sufficient to achieve slow migration, uniform distribution over the emitter cap is rapidly achieved but equilibration between the shank and emitter is achieved much more slowly. Equilibration without concomitant desorption is especially difficult to attain at high Cs coverages because of the small difference between equilibration and desorption temperatures. This problem is still more serious for W/O and W/F substrates because these two electronegative adsorbates increase the migration temperature of Cs for coverages less than one monolayer. The equilibration problem was solved by dosing the emitter with \( \geq 3 \) separate monolayers\(^{50} \) and equilibrating the emitter cap with each one before equilibrating for 10 minutes at \( \sim 300^\circ\text{K} \). Working coverages of Cs were then established by desorbing off excess Cs at the appropriate temperature. Failure to employ this procedure resulted in either curved Arrhenius plots or Arrhenius constants representative of diffusion processes.

Dosing the emitter with O\(_2\) and CsF was accomplished by heating the Pt buckets enclosing CuO or CsF respectively. The required W/O or W/F surface was then obtained by heating the dosed surfaces in the neighborhood of 1100-1200\(^{\circ}\text{K}\) in order either to remove loosely bound O and F or to con-
vert these to tighter binding states. This is necessary to minimize subse-
quent adsorbate desorption and state change which would otherwise occur
during cesium desorption runs at elevated temperatures. Such changes
would obscure interpretation of desorption data and so must be avoided. The
Cs accompanying the initial deposition of F was of course also removed by
heating the emitter to 1100-1200°K. Build-up of large amounts of F on the
surface required as many as 5-6 repetitions of this dosing/heating sequence.
Maximum F retention on the surface was accomplished by dosing the emitter
with CsF and heating it to 1100°K with the field emission tube screen held at
-200 V during the last few dosing sequences.

The method used for obtaining work functions is based on the analysis
presented earlier in Section I, page 7. In the present case $\beta_{rel}/\beta_{av} = 1$ and
\( \phi \) is given by

$$\phi_a = \left( m_a/m_{c'} \right) \phi_{c'}$$

(19)

where the subscripts \( c' \) and \( a \) refer to clean and adsorbate covered emitters
respectively. Adsorbate coverage was measured by first determining work
functions and then using this to obtain coverage from previously obtained work
function/adsorbate coverage curves. An auxiliary method of monitoring cov-
erage involved measuring the voltage \( V \) required to draw a fixed field emis-
sion current and using \( V \) as an indicator of surface coverage instead of \( \phi \).
This method was especially useful for collecting desorption data.
Field Emission Probe Techniques for Measuring Binding Energies of Cesium on Single Crystal Planes

Three field emission methods of obtaining binding energies of Cs on various substrates are available. These three methods each involve use of probe hole techniques in which the electrons field emitted from a single plane are collected in a Faraday cup collector, but the methods differ in quantities directly measured and interpretation. A description of the methods is described below:

(1) Measuring\textsuperscript{50,51} the equilibrium distribution of Cs over the substrate and obtaining differences in heats of binding between the different planes from the Boltzmann equation: \( n_1/n_2 = \exp (F_2 - F_1)/kT \), where \( n_1 \) and \( n_2 \) are the concentrations of Cs on planes 1 and 2 and where \( F_1 \) and \( F_2 \) are the corresponding free energies of desorption. A reasonable assumption, especially at low coverages, is that differences in entropy of desorption are negligible so that \( F_2 - F_1 \approx H_2 - H_1 \) where \( H_2 \) and \( H_1 \) are the enthalpies of desorption of Cs from planes 1 and 2 respectively. The quantity \( H_2 - H_1 \) may be obtained as a function of average surface coverage, \( \bar{n} \), by measuring \( n_1/n_2 \) as a function of \( \bar{n} \). At coverages, \( \theta \geq 0.3 \), \( n_2/n_1 \) for all planes tends to unity so that enthalpies of adsorption for the different planes converge to the same value - that measured in experiments which relate average enthalpies, \( \bar{H} \) of desorption to average coverage of Cs. For the case where \( \bar{H} \) increases as \( \bar{n} \) decreases, \( \bar{H} \) corresponds to value of \( H \) for the plane which binds Cs the most strongly. For Cs
adsorbed on clean tungsten, this is the (110) plane. Hence by determining
the ratios \( n_i / n_{110} \) for all other planes, we can establish \( H_i \) as a function
of \( \tilde{n} \) for each of them. The procedure used to measure \( n_i \) as a function of
\( \tilde{n} \) depends on how Cs affects either \( \phi_i \), the work function of plane \( i \) or \( V_i \),
the voltage required to reach a given fixed current \( I_0 \) for the plane. In
either case the task involves obtaining work function versus coverage curves
for Cs deposited both in an equilibrated state and in an unequilibrated state
in which the distribution of Cs depends only on the number of Cs atoms
which impinge on each plane during dosing and not on how the energy of
adsorption of Cs varies from plane to plane. (Note that no activation
energy of adsorption is involved when Cs is adsorbed on W so that energy
of adsorption = energy of desorption.) Cs dosing is accomplished by direc-
ting a flux of Cs atoms along a line which makes as small an angle \( V \sim 30^\circ \)
as possible to the emitter axis. The relation between impinged adsorbate
density, \( n_i \), and \( \tilde{n} \) is given by: \( n_i / \tilde{n} = \pi (\cos \epsilon' \sin \gamma) \), where \( \epsilon' \) is the angle
between the Cs source and the normal to the region \( i \) being probed. Cs
average coverage \( \tilde{n} \) is obtained by determining the work function change \( \Delta \tilde{\phi} \)
for 1, 2, \ldots \, n equilibrated doses of Cs and comparing the results with previous-
ly obtained curves of \( \Delta \tilde{\phi} \) versus \( \tilde{n} \) for Cs on W. Curves of \( \phi_i \) versus \( \tilde{n} \) for
equilibrated and \( \tilde{\phi}_i \) versus \( \tilde{n} \) for unequilibrated layers may be combined to
yield information on how \( n_i \) varies with \( \tilde{n} \) by noting that a work function \( \phi_i \)
corresponds to \( \tilde{n} \) on the equilibrated curve and to \( n_i \) on the unequilibrated plot.
The unequilibrated curve is used as a calibration curve and enables us to
convert measured work function values, obtained from the equilibrated
curves into actual surface coverages which exist as a result of equili-
bration. This procedure is repeated for other planes of interest to ob-
tain the ratios of \( n_i/n_{110} \) from which the enthalpies \( H_i \) are obtained.

(2) In this method, use is made of the Boltzmann relation above \( n_i/n_2 = \exp (F_i - F_2)/kT \) except that \( \ln(n_1/n_2) \) is plotted as a function of \( 1/T \) to yield \( F_1 - F_2 \) directly without the use of the unequilibrated curves.

Now \( \Delta \theta_i \propto n_i \) at least for small coverages and to a good approximation \( (\Delta V_i/V_{oi}) \propto n_i \) where \( V_{oi} \) is the voltage required to draw a fixed re-
ference current \( I_0 \) and \( \Delta V_i \) is the change in that voltage caused by Cs
deposition. Hence we have \( \ln(\Delta V_1/V_{o1})/(\Delta V_2/V_{o2}) = \text{constant} + \)
(\( H_i - H_2)/kT \) so that a plot of \( \ln(\Delta V_1/V_{o1})/(\Delta V_2/V_{o2}) \) versus \( 1/T \)
should yield \( H_1 - H_2 \) whereas the previous method yields \( F_1 - F_2 \). The
procedure involves heating the cesium coated emitter at a temperature
\( T \) until equilibrium is attained and then cooling rapidly to quench in this
distribution which is determined by sampling \( \Delta V \) for planes of interest.
This is repeated for other values of \( T \). If the equilibration temperature
chosen is too high, the Cs will rearrange on cooling to give a distri-
bution characteristic of a lower temperature \( T_H \). If the equilibration
temperature chosen is too low, impossibly long equilibration times will
be required. Whether or not the method is practicable depends on the
time constant, \( T_C \), for cooling the emitter and on the width of the tem-
perature zone \( T_H - T_L \) where \( T_L \) is the temperature for which equili-
bration times \( \gtrsim 10^4 \text{s} \). Large values of \( T_C \) are inconvenient since
they decrease \( T_H - T_L \) by decreasing \( T_H \).
(3) This method is a variant of the first method in which a simple model is assumed for variation of dipole moment, \( \mu \), with coverage; local coverage \( \Theta_i \) may then be found from the Helmholtz equation

\[
\phi_i = 4\pi \mu n_o \Theta_i
\]

where \( \phi_i \) is the work function change on plane \( i \) due to adsorption of Cs and \( n_o \) is the surface density of adsorbate when \( \Theta_i = 1 \). Gomer et al. \( 52 \) found that the Topping \( 53 \) depolarization model was adequate to explain how \( \mu \) varied with \( \Theta_i \) whereas Swanson and Strayer \( 54 \) found that a simple empirical representation worked just as well. Both models contain two adjustable constants which can be evaluated by fitting to experimental data at the minimum of the work function coverage curve.

The justification for this procedure is based on Gomer's \( 51 \) finding that no coverage anisotropy existed at the minimum point for the closely analogous tungsten/potassium system.

Although all the above three methods offer means of obtaining values of \( H \) for individual planes, each offers a different balance of convenience and certainty. The first and third methods enable us to compute values of \( F_2 - F_1 \) from which \( H_2 - H_1 \) is obtained by the reasonable assumption that \( F_2 - F_1 = H_2 - H_1 \). The second method is free of this assumption and \( H_2 - H_1 \) is calculated directly from \( I/V \) measurements for planes 1 and 2. In the low adsorbate coverage range this method does not require knowledge of \( \mu_1(\Theta = 0) \) and \( \mu_2(\Theta = 0) \); at high coverages it still may be used provided the relations \( \Delta \phi_1(\Theta_1) \) and \( \Delta \phi_2(\Theta_2) \) are known. These may be obtained from unequilibrated data as in method (1). Methods (1) and (3) have been successfully tried be-
however, we selected method (2) for investigation because not only does it offer us a direct measure of $H_2 - H_1$ and hence $H$ for any plane but in the low coverage region where $H_2 - H_1$ is likely to be greatest, the method does not require knowledge of how $\Delta \theta_i$ varies with $\theta_i$.

The field emission tube used in this section is shown in Fig. 14. It contains a quadrupole electrostatic deflection system, a CuO oxygen source and a cesium zeolite ion source. The deflection system was operated with opposite quadrants raised equal voltages above and below the anode potential. Operation of the deflection system did not introduce any field corrections, provided the emitter was well centered.

The method involves depositing cesium on the emitter and heating at temperature $T_1$ until thorough equilibration of the cesium over the emitter and its shank has been achieved. The emitter is then cooled to quench in the cesium distribution which is determined from the I/V characteristics of the planes of interest. Equilibration is next resumed at a lower temperature $T_2$ and the quenched in cesium is determined once more. This procedure is repeated until the quenched in distribution is changed.

Unfortunately, no such change has yet been confirmed, even after a detailed search of the temperature range between 300°K and 160°K. Some initial changes were noted on the 100 and 110 plane but these were not erased by reheating to 300°K so that the coverage changes were not reversible. The failure to successfully implement this method so far may be due to one or more of the following reasons:

1. The upper temperature at which equilibration was begun was
Figure 14. Cross section of electrostatic deflection probe tube.
too low in which case equilibration would not occur in the time of experiment.

(2) The lower temperature at which equilibration was terminated may have been too high in which case rearrangement of adsorbate would have occurred during quenching of the emitter to 780K.

(3) The quench time of the emitter was too long so that the difference $T_H - T_L$ was too small. Very small values of $T_H - T_L$ could hinder the search for changes of adsorbate distribution with temperature because the experimental procedure involved decreasing the emitter temperature in a series of discrete steps. If the size of these temperature steps was greater than $T_H - T_L$, the critical equilibration zone between $T_H - T_L$ could easily be missed. Possibility (3) was checked by measuring the emitter loop temperature as a function of time after heating to various temperatures.

Although longer than expected (see Fig. 15), the quench time is still small enough for an adequate temperature range $T_H - T_L$. The quench time measured here is for the loop. Rough calculations indicate the emitter temperature is capable of following the loop temperature quite closely since the time required for the emitter to cool to 1/2 of the temperature difference between it and the point where the shank joins the loop is about 0.1 seconds.

By referring to earlier data on Cs diffusion times for various regions of the W emitter the temperature zone $T_H - T_L$ was established at $\sim 30^\circ$K in the
Figure 15. Figure shows how temperature of emitter dropped when heating current was terminated.
temperature range 200-250°K. However, some O was deposited along with
Cs during dosing so that actual equilibration temperatures may have been
higher than those investigated so far.

**Methods of Data Analysis**

It was assumed that desorption took place according to first order kine-
tics in which case:

\[
k = -d \frac{\Theta}{dt} = v \exp \left(-\frac{H}{kT}\right)
\]

(20)

where \( v \) is the preexponential of desorption. \( H \) varies with surface coverage \( \Theta \). Swanson and Gomer have discussed this situation and the following ana-
lysis is based on their work. Over a small range of coverage, \( H(\Theta) \) may be
represented by:

\[
H(\Theta) = H(\Theta_i) + g(\Theta - \Theta_i)
\]

(21)

where \( g = \delta H/\delta \Theta \). Hence we have:

\[
-d \frac{\Theta}{dt} = v \Theta \exp \left[-\frac{H(\Theta_i)}{kT}\right] \exp \left[-\frac{g(\Theta - \Theta_i)}{kT}\right]
\]

\[
= k_i \exp \left[-\frac{g(\Theta - \Theta_i)}{kT}\right] \text{ say.}
\]

(22)

On integration we have:

\[
k_i t = \exp \left(-\frac{g \Theta_i}{kT}\right) \int_{\Theta_f}^{\Theta_i} \exp \left(\frac{g \Theta}{kT}\right) d\Theta
\]

(23)

where \( \Theta_i \) and \( \Theta_f \) are the surface coverages at time 0 and time t respectively.
If the variation in $\Theta^{-1}$ can be neglected through the interval $\Theta_f - \Theta_i$, then the integration of Eq. (23) can be given in closed form. This requirement is that

$$|g|/kT >> \Theta^{-1}$$

(24)

and this just holds for the results obtained in this work. Finally if

$$\exp \left( (\Theta_f - \Theta_i)/kT \right) >> 1$$

(25)

we have for $g < 0$ (i.e., $H_{des}$ increases as $\Theta$ decreases)

$$k_f = kT/(\Theta_f \cdot |g| t).$$

(26)

Both of the above inequalities hold for this work so that from Eqs. (20) and (26) we have:

$$\exp [-H(\Theta_f)/kT] = kT/(\Theta_f |g| t)$$

(27)

so

$$-H(\Theta_f)(\log_{10}e)/kT = \log kT/(\Theta_f |g|) - \log t$$

(28)

hence

$$\delta \log t/\delta (1/T) = H(\Theta_f) \log_{10}e/k = S$$

(29)

Hence the slope $S$ of an Arrhenius plot of $\log t$ versus $1/T$ yields the greatest value of $H$ during the interval $\Theta_f - \Theta_i$. The preexponential term $\log \nu$ is obtained from Eqs. (28) and (29) and is given by

$$\log \nu = S/T + \log \{ kT/\Theta_f |g| \} - \log t.$$
Values of \( g \) were obtained from plots of \( H \) versus \( \Theta \). At some coverage points \( H \) was obtained from a desorption run at one temperature in which case a value for \( \log V \) was assumed. Neutral atom desorption was ensured during high temperature runs by biasing the field emission screen positively. By biasing the screen negatively, both ionic and neutral desorption products were obtained. Checks for removal of electronegative adsorbate during Cs desorption were carried out by using the latter electric field regime. Terminal desorption in this situation was a regenerative process so that Cs could be removed at significantly lower temperatures than for the neutral desorption case. Under these conditions, Cs was removed with minimal further effect on the underlying electronegative layer.

Results of Cesium Desorption from Fluorinated Tungsten

Table VII summarizes the ionic and neutral desorption energies and preexponential results obtained at different coverages of Cs on two W/F substrates. A plot of \( H \) versus \( n \) is depicted in Fig. 16 along with a plot\(^{57}\) of \( H \) versus \( n \) for Cs on clean W. It can be seen that values of \( H \) converge to the clean W values for \( n = 1 \times 10^{18} \) atoms/m\(^2\), and, within the limits of experimental error, are indistinguishable from one another for the two F coverages studied in this work. An interesting feature of the Table VII results is the similarity (mostly within \( \pm 10\% \)) between the values of \( H \) and those of the corresponding work functions. For \( n = 1 \times 10^{18} \) atoms/m\(^2\), the values of \( H \) for W/F substrates are about 0.5 eV larger than the clean W
<table>
<thead>
<tr>
<th>Initial substrate work function eV</th>
<th>Cesium coverage atoms/m²</th>
<th>Cesium substrate work function (eV)</th>
<th>Activation energy of desorption (eV)</th>
<th>Log (desorption preexponential)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.78</td>
<td>(1.18-1.31) x10¹⁸</td>
<td>1.85</td>
<td>2.08&lt;sup&gt;ac&lt;/sup&gt;</td>
<td>14.0</td>
</tr>
<tr>
<td>4.78</td>
<td>(0.72-0.88) x10¹⁸</td>
<td>2.35</td>
<td>2.48&lt;sup&gt;c&lt;/sup&gt;</td>
<td>13.7</td>
</tr>
<tr>
<td>4.78</td>
<td>(0.50-0.65) x10¹⁸</td>
<td>2.84</td>
<td>3.38&lt;sup&gt;c&lt;/sup&gt;</td>
<td>17.3</td>
</tr>
<tr>
<td>4.78</td>
<td>(0.50-0.65) x10¹⁸</td>
<td>2.84</td>
<td>2.82&lt;sup&gt;ac&lt;/sup&gt;</td>
<td>14.0</td>
</tr>
<tr>
<td>4.78</td>
<td>(0.34-0.39) x10¹⁸</td>
<td>3.44</td>
<td>3.39&lt;sup&gt;c&lt;/sup&gt;</td>
<td>16.2</td>
</tr>
<tr>
<td>4.78</td>
<td>(0.34-0.39) x10¹⁸</td>
<td>3.44</td>
<td>3.02&lt;sup&gt;ac&lt;/sup&gt;</td>
<td>14.0</td>
</tr>
<tr>
<td>5.22</td>
<td>(2.42-2.48) x10¹⁸</td>
<td>1.46</td>
<td>1.35&lt;sup&gt;c&lt;/sup&gt;</td>
<td>12.3</td>
</tr>
<tr>
<td>5.22</td>
<td>(1.47-1.53) x10¹⁸</td>
<td>1.42</td>
<td>1.75&lt;sup&gt;c&lt;/sup&gt;</td>
<td>12.9</td>
</tr>
<tr>
<td>5.22</td>
<td>(0.90-1.30) x10¹⁸</td>
<td>2.04</td>
<td>2.54&lt;sup&gt;c&lt;/sup&gt;</td>
<td>14.0</td>
</tr>
<tr>
<td>5.22</td>
<td>(0.90-1.30) x10¹⁸</td>
<td>2.04</td>
<td>2.40&lt;sup&gt;ac&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>5.22</td>
<td>(0.70-0.80) x10¹⁸</td>
<td>2.72</td>
<td>2.83&lt;sup&gt;c&lt;/sup&gt;</td>
<td>13.7</td>
</tr>
<tr>
<td>4.99-5.59&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.13 x 10¹⁸</td>
<td>4.28</td>
<td>3.72&lt;sup&gt;ac&lt;/sup&gt;</td>
<td>14.0</td>
</tr>
</tbody>
</table>

**Atoms**

**Ions**

| 5.05                        | (0.14-0.04) x10¹⁸ | 4.50 - 4.90 | 1.88<sup>d</sup>  | 9.9             |
| 4.66                        | (0.09-0.04) x10¹⁸ | 4.40 - 4.60 | 2.20<sup>d</sup>  | 11.6            |

<sup>a</sup>Activation energy of desorption calculated by assuming a desorption preexponential of 10<sup>14</sup>.

<sup>b</sup>Note that F concentration was diminishing during course of run.

<sup>c</sup>Neutral cesium atom desorption was ensured by applying +50 V to screen during desorption process when T > 600°K.

<sup>d</sup>Ionic desorption was assisted by making the screen -50 V.
Figure 16. Plots of activation energies of Cs neutral desorption from two W/F substrates. The symbol ■ represents data from a W/F surface of initial work function of 5.22 eV, while ○ denotes desorption from a surface of initial work function 4.78 eV. The solid line which terminates at \( n = 0, H_{\text{des}} = 3.3 \) eV, represents desorption from a clean W surface.
values. For initial W/F work functions greater than 4.8 eV, activation energy measurements for desorption of Cs neutrals were restricted to Cs coverages greater than $0.7 \times 10^{18}$ atoms/m$^2$ because removal of F by cesium takes place at the higher temperatures required to desorb Cs from lower Cs coverages. For initial W/F work functions around 4.8 eV, desorption was restricted for the same reason to Cs coverages of greater than $0.3 \times 10^{18}$ atoms/m$^2$. A final desorption curve obtained at 1000°K for neutral Cs desorption was accompanied by removal of F; an initial W/F work function of 4.99 eV declined to 4.59 eV after desorption. Cs coverage information was obtained from previously published work function/coverage curves for Cs adsorbed on various W/F substrates. \textsuperscript{52}

When the measured desorption preexponential exceeded $10^{15}$, H was recomputed from the Arrhenius plot by assuming a value for the preexponential of $10^{14}$. These values are included in Table VII and in Fig. 15 where they are represented by open symbols.

Two ionic heats of desorption were also measured at low Cs coverages from W/F substrates of work functions 4.66 eV and 5.05 eV. Both H and log v were similar to the clean W values measured by Gomer and Schmidt.

Complete removal of Cs as neutral atoms from W/F substrates appeared to be accompanied by near total removal of F from the substrate, at least for the temperatures studied so far. Complete removal of Cs ions, however, was not accompanied by F removal, provided, of course, that the initial Cs covered substrate work function was high enough for Cs
to come off in ionic form. The data in Table VIII summarizes these findings and indicates a final W/F work function of 4.60 after prolonged desorption of Cs as neutrals at temperatures up to 1000°K. At this point the field emission pattern was very similar to the clean W one. Additional work on desorption of Cs as neutrals at 1100°K also indicated concomitant removal of F.

Results of Cesium Desorption from Oxygenated Tungsten

The activation energies and preexponential results for Cs desorption from oxygenated W substrates are summarized in Table IX and depicted in Fig. 17.

For complete desorption of Cs neutrals from O/W substrates without concomitant removal or rearrangement of the adsorbed O, it is necessary to preheat the O/W surfaces to at least the maximum temperature necessary to remove Cs neutrals. If this is done, then the maximum work function of the O/W surface is restricted to less than about 4.8 eV. This is illustrated in Fig. 18 which depicts the decline of work function with temperature for two O/W surfaces. It is apparent from Fig. 18, that in the temperature range of interest, an initial coverage of O characterized by $\Delta \phi = 0.2$ eV is sufficient to allow development of the same $\phi/T$ features as higher initial O coverage curves. The two O/W surfaces chosen in this work were characterized by the work functions 4.32 eV and 4.72 eV; the former was obtained by heating a 78°K deposited O/W layer to 1400°K and the latter by heating it to 1200°K. The 4.32 eV O/W surface was more stable than the 4.72 eV surface; thus,
TABLE VIII - EFFECT OF CESIUM DESORPTION CONDITIONS ON STABILITY OF ADSORBED FLUORINE.

<table>
<thead>
<tr>
<th>Initial Cs free W/F work function - eV</th>
<th>Initial W/F/Cs work function eV</th>
<th>Heating treatment during neutral desorption (screen at +50 V)</th>
<th>Final W/F/Cs work function eV</th>
<th>Final Cs free W/F work function - eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.15</td>
<td></td>
<td>920°K, 1000 sec.</td>
<td>4.00</td>
<td>4.72</td>
</tr>
<tr>
<td>4.72</td>
<td></td>
<td>920°K, 800 sec.</td>
<td>3.92</td>
<td>4.76</td>
</tr>
<tr>
<td>4.76</td>
<td>2.0</td>
<td>920°K, 1000 sec.</td>
<td>4.00</td>
<td>4.68</td>
</tr>
<tr>
<td>4.68</td>
<td></td>
<td>1000°K, 1000 sec.</td>
<td>4.50</td>
<td>4.61</td>
</tr>
<tr>
<td>4.61</td>
<td></td>
<td>1000°K, 1000 sec.</td>
<td>--</td>
<td>4.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ionic desorption screen at -50 V.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.06</td>
<td>4.0</td>
<td>840°K, 80 sec.</td>
<td>5.04</td>
<td>5.04</td>
</tr>
</tbody>
</table>

a Cs remaining on W/F substrate after partial removal of Cs as neutrals was removed as ions in 20 seconds at 900°K -- screen at +50 V.
TABLE IX - ACTIVATION ENERGIES AND PREEXPONENTIALS OF DESORPTION OF CESIUM NEUTRALS\textsuperscript{a} FROM OXYGENATED TUNGSTEN SUBSTRATES.

<table>
<thead>
<tr>
<th>Initial Substrate Work Function eV</th>
<th>Cesium Coverage atoms/m\textsuperscript{2}</th>
<th>Cesium Covered Substrate Work Function eV</th>
<th>Activation Energy of Desorption eV</th>
<th>Log (Desorption Preexponential)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.32</td>
<td>$0.71 \times 10^{18}$</td>
<td>2.0</td>
<td>3.18</td>
<td>17.0</td>
</tr>
<tr>
<td>4.32</td>
<td>$0.71 \times 10^{18}$</td>
<td>2.0</td>
<td>2.70\textsuperscript{a}</td>
<td>14.0</td>
</tr>
<tr>
<td>4.32</td>
<td>$0.51 \times 10^{18}$</td>
<td>2.7</td>
<td>3.61</td>
<td>16.2</td>
</tr>
<tr>
<td>4.32</td>
<td>$0.51 \times 10^{18}$</td>
<td>2.7</td>
<td>3.08\textsuperscript{a}</td>
<td>14.0</td>
</tr>
<tr>
<td>4.32</td>
<td>$0.20 \times 10^{18}$</td>
<td>3.6</td>
<td>3.61</td>
<td>14.5</td>
</tr>
<tr>
<td>4.32</td>
<td>$0.03 \times 10^{18}$</td>
<td>4.1</td>
<td>4.18</td>
<td>15.2</td>
</tr>
<tr>
<td>4.72</td>
<td>$2.49 \times 10^{18}$</td>
<td>1.9</td>
<td>0.80</td>
<td>14.1</td>
</tr>
<tr>
<td>4.72</td>
<td>$1.25 \times 10^{18}$</td>
<td>1.3</td>
<td>1.78</td>
<td>12.0</td>
</tr>
<tr>
<td>4.72</td>
<td>$0.75 \times 10^{18}$</td>
<td>2.0</td>
<td>2.84</td>
<td>13.6</td>
</tr>
<tr>
<td>4.72</td>
<td>$0.46 \times 10^{18}$</td>
<td>2.8</td>
<td>3.08</td>
<td>12.8</td>
</tr>
<tr>
<td>4.72</td>
<td>$0.20 \times 10^{18}$</td>
<td>3.6</td>
<td>3.92</td>
<td>15.3</td>
</tr>
<tr>
<td>4.72</td>
<td>$0.10 \times 10^{18}$</td>
<td>4.2</td>
<td>3.96\textsuperscript{b}</td>
<td>14.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} These activation energies were recalculated from the Arrhenius plots by assuming $\log v = 14$.

\textsuperscript{b} This terminal energy was estimated from one temperature desorption curve by assuming $\log v = 14$; concomitant removal of $O_2$ during desorption vitiated the Arrhenius results.
Figure 17. Plots of activation energies of Cs neutral desorption from two different W/O substrates. The symbol ■ corresponds to a surface of initial work function of 4.32 eV while the symbol ○ corresponds to desorption from a surface of initial work function of 4.72 eV. The solid, initially lower, curve represents Cs desorption from clean W.
Figure 18. Plot of work function change resulting from heating a partially covered W emitter for 60 seconds at progressively increasing temperatures. Note beyond 1200°K, the curves essentially overlap.
the former surface did not undergo further work function change even after repeated 1100°K removal of Cs neutrals; while the 4.72 eV surface slowly decreased in work function after terminal desorption of Cs neutrals. Because of this no Arrhenius plot could be established for the terminal desorption; instead the energy in this case was estimated by assuming \( \log v = 14 \) in Eq. (32). The W/O surfaces studied here differ from their F analogues in that desorption of O is not catalyzed by the Cs desorption process; the change in W/O work function which occurred after prolonged high temperature removal of Cs neutrals from the 4.72 eV O/W surface continued when the Cs free surface was again heated at 1100°K. Clearly the absence of Cs promoted removal of electronegative adsorbate in the case of the Cs/O/W system is the major difference from the Cs/F/W system.

The high temperatures to which the O/W and F/W surfaces were pre-heated was sufficient to cause reconstruction of the surfaces so that adsorption of Cs takes place on surfaces which are poorly characterized from a chemisorption point of view. In the case of O/W the high temperature processing is sufficient to cause formation of at least partially oxidized surfaces.

The curves of \( H \) versus \( n \) for the Cs/O/W system are similar to those of the Cs/F/W system; as in the F case, \( H \) does not strongly depend on the concentration of underlying electronegative adsorbate, at least for the range of O coverages studied in this work. In the lower coverage range of adsorbed Cs (\( n < 1 \times 10^{18} \) atoms/m\(^2\)), \( H \) is similar for both the Cs/O/W and the Cs/F/W systems. Above \( n = 1 \times 10^{18} \) atoms/m\(^2\), \( H \) is significantly below the values for the clean W substrate.
A noteworthy feature of the work function versus temperature curve for the Cs/O/W system is that for an initial apparent O/W work function of 4.32 desorption at progressively higher temperatures leads to a minimum in the $\Phi$ versus $T$ curve at 600°K of 0.75 eV.

Discussion of Results of Cesium Desorption from Oxygenated Tungsten and from Fluorinated Tungsten

The curves of $H$ versus $n$ are remarkably similar for the two coadsorbate systems except, perhaps, at high coverage values of Cs where, on the basis of a single experimental data point, the Cs/O/W curve lies somewhat below that of the Cs/F/W curve. Inclusion of additional data points in the Cs coverage region between 1.2 and $2.5 \times 10^{18}$ atoms/m² would possibly have resulted in greater similarity between the two curves in the high Cs coverage range. Convergence of values of $H$ at very high Cs coverages is expected to occur between the curves of $H$ versus $n$ for the systems Cs/O/W, Cs/F/W and Cs/W. This is because at high coverages of Cs, the effect of the substrate will be masked out and $H$ will drop to the sublimation energy of Cs from Cs. Within the limits of experimental error, there is no significant difference between the curves of different initial coverage of electronegative adsorbate. Because of the difficulty in depositing contaminant free CsF, the above results raise an element of uncertainty about the low coverage Cs/F/W results; it is conceivable that the presence of a small amount of O was responsible for the similarity between the Cs/O/W and Cs/F/W results.
at low coverage. Evidence against the presence of concomitant deposition of O along with CsF is as follows: the CsF was carefully protected from air in a N2 filled air bag prior to insertion inside the field emission microscope, and was then carefully outgassed before use; in addition the field emission pattern after near complete Cs promoted removal of F at 1000°K from W was hardly distinguishable from that of clean W. Since Cs does not promote removal of O at 1000°K, any O deposited along with the F would have remained after the F had been removed and would have revealed its characteristic pattern. Consequently it is felt that no significant amounts of O were codeposited with F.

It is interesting to speculate about the reason why the H/n curves for Cs/O/W and Cs/F/W decline more sharply than the Cs/W system curve. Schmidt and Gomer50, 51 have discussed the decline in H for the Cs/W system and find that for \( n \leq 1.4 \times 10^{18} \text{ atoms/m}^2 \), the decrease in H may be accounted for by increasing electrostatic repulsion between the adparticles as they crowd closed together. The decrease, \( \Delta H \), is given by51

\[
-\Delta H = g' c(d_0, n) \Delta \phi
\]  

(31)

where \( g' \) is the charge per adatom, \( \Delta \phi \) the contact potential resulting from the adsorbate, and \( c(d_0N) \) a function of adsorbate density and size which relates the contact potential to the potential actually existing at an adsorbate site. On the basis of \( g' = 1 \), Schmidt and Gomer were able to explain the variation in H with \( \Theta \) for Cs/W. Although these authors felt that \( g' < 1 \), this was compensated by a greater than average value of \( n \) for certain planes such as...
In the case of the composite systems Cs/O/W and Cs/F/W, $\Delta \phi$ is larger than for the Cs/W system and $\Delta H$ at $n = 1 \times 10^{18}$ atoms/cm$^2$ increases in the same qualitative order as $\Delta \phi$ as may be seen below.

### TABLE X - CORRELATION OF $\Delta H = H(n = \infty) - H(n = 1.0 \times 10^{18}$ ATOMS/cm$^2$) WITH $\Delta \phi$ at $n = 1 \times 10^{18}$ FOR THE SYSTEMS Cs/W, Cs/F/W and Cs/O/W.

<table>
<thead>
<tr>
<th>System</th>
<th>Cs/W</th>
<th>Cs/F/W</th>
<th>Cs/O/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$(eV)</td>
<td>1.0</td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td>$\Delta \phi$(eV)</td>
<td>2.5</td>
<td>3.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

However, the electrostatic repulsion does not account for all of $\Delta H$ at $1.0 \times 10^{18}$ atoms/m$^2$ and additional explanations must be invoked. The terminal desorption heats of Cs are greater than the clean W value by $0.6 \pm 0.3$ eV for the Cs/F substrate and $0.9 \pm 0.3$ eV for the Cs/O substrate. The fact that F and O can increase the terminal values of H is not surprising since at low Cs coverage, Cs should be adsorbed in ionic form while the adsorbed O or F should be bonded with an appreciable degree of ionicity, consequently the electrostatic interaction of Cs with the surface should be larger when electronegative gases are pre-adsorbed than with the clean W substrate.

The reproducible, very low work function of 0.75 eV which was obtained by heating to $600^\circ$K multilayers of Cs adsorbed on an O/W layer of initial work function of 4.32 eV is worthy of note. At least part of the low work
function is probably due to build up and rearrangement of the bright 111, planes which combine to produce an anomalously high local field factor $\beta$, where $\beta = F/V$, $F$ being local electric field and $V$ the applied voltage. It seems likely however that the real local work function for Cs/O/W on the 111 plane is still significantly less than 1 eV because in order for the real average Cs/O/W work function to be 1 eV instead of 0.75 eV the Cs free O/W work function would have to be 5.75 eV instead of 4.32 eV and this seems unlikely.

Results of Single Plane Adsorption Energies of Cesium on Rhenium

The terminal desorption energy of Cs neutrals from Re was determined from an Arrhenius plot to be 3.0 eV while the corresponding preexponential was found to be 11.6. Desorption energies at other coverages (Fig. 19) were determined from plots of Cs coverage versus 60 second heating temperatures. This latter plot shown in Fig. 20 was obtained from a plot of $\phi$ versus temperature (Fig. 21) and a previously determined plot of $\phi$ versus coverage (Fig. 22).

Single plane binding energies of Cs on Re for the 1012 and 1014 planes were determined by the method (1) and described in section I, p. 63. $\phi$ versus Cs coverage plots were obtained both for equilibrated and unequilibrated Cs doses, the latter to convert equilibrated work function changes into Cs coverages on each plane studied. Plots of $\Delta \phi$ versus $\bar{n}$, average adsorbate density are depicted in Figs. 23, 24, and 25, while values of $n_i$ ($i = 1012,$
Figure 19. Plot of Cs neutral desorption energy from Re versus average surface coverage.
Figure 20. Plot of average Cs coverage on Re as a function of 60 second heating temperature.
Figure 21. Plot of work function versus temperature for Cs adsorbed on Re; 60 second heating times were used.
Figure 22. Plot of work function versus average Cs coverage for Cs on Re.
Figure 23. Plots of equilibrated and unequilibrated Cs layers adsorbed on (1012) Re planes.
Figure 24. Plots of equilibrated and unequilibrated Cs layers adsorbed on (0001) Re planes.
Figure 25. Plots of equilibrated and unequilibrated Cs layers adsorbed on (10\overline{1}4) Re planes.
0001, and 10\overline{1}4) versus \( \bar{n} \) are shown in Table XI from which ratios of \( n_1/n_{0001} \) could be obtained. The 0001 and 10\overline{1}2 planes were assumed to be the tightest binding planes for Cs and since, when equilibrium is maintained during desorption, the binding energy is weighted towards the highest desorption energy plane, we assumed that the plot of average desorption energy \( \bar{n} \) represented H for these planes. Desorption energies for the 0001, 10\overline{1}4, and the 10\overline{1}2 plane are shown in Table XII at various values of \( n \). The maximum difference in binding energy occurs at \( \bar{n} = 0.1 \times 10^{18} \) atoms/m\(^2\) on the 10\overline{1}4 plane (a relatively bright plane) and only amounts to 0.03 eV. Between the two dark planes 0001 and 10\overline{1}2, the maximum difference is only 0.003 eV at \( \bar{n} = 0.1 \times 10^{18} \) atoms/m\(^2\). The values of H versus \( \bar{n} \) for the different planes may be converted into values of H versus actual surface concentration \( n \) with the aid of Table XII, which shows how \( n \) for each plane studied varies with \( \bar{n} \).

**Discussion**

The differences in binding energy between the planes of Re studied so far is comparable to that between the 110 and 100 planes of W (0.05 eV at \( \bar{n} \sim 0.05 \times 10^{18} \) atoms/m\(^2\)). Schmidt and Gomer\(^57\) have pointed out that in an equilibrium situation when several planes compete for adsorbed Cs, the Cs distributes itself in a manner which nearly equalizes the binding energy on each plane. This occurs in order to minimize the overall free energy of the metal/Cs system. In spite of small anisotropies of the desorption ener-
TABLE XI - ACTUAL CESIUM CONCENTRATIONS (\( \cdot \)) FOR THE 0001, 10\( \overline{1}4 \) AND 10\( \overline{1}2 \) PLANE OF RHENIUM VERSUS AVERAGE CESIUM CONCENTRATION ON RHENIUM FIELD EMITTER.

<table>
<thead>
<tr>
<th>Average Cs concentration ( \bar{n} ) atoms/m(^2) ( x10^{18} )</th>
<th>Cs concentration on the 0001 plane ( (n_{000}) ) atoms/m(^2) ( x10^{18} )</th>
<th>Cs concentration on the 10( \overline{1}4 ) plane ( (n_{10\overline{1}4}) ) atoms/m(^2) ( x10^{18} )</th>
<th>Cs concentration on the 10( \overline{1}2 ) plane ( (n_{10\overline{1}2}) ) atoms/m(^2) ( x10^{18} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>0.017</td>
<td>0.005</td>
<td>0.035</td>
</tr>
<tr>
<td>0.010</td>
<td>0.036</td>
<td>0.010</td>
<td>0.065</td>
</tr>
<tr>
<td>0.013</td>
<td>0.052</td>
<td>0.013</td>
<td>0.080</td>
</tr>
<tr>
<td>0.020</td>
<td>0.070</td>
<td>0.020</td>
<td>0.095</td>
</tr>
<tr>
<td>0.050</td>
<td>0.160</td>
<td>0.050</td>
<td>0.170</td>
</tr>
<tr>
<td>0.070</td>
<td>0.207</td>
<td>0.070</td>
<td>0.200</td>
</tr>
<tr>
<td>0.1</td>
<td>0.27</td>
<td>0.1</td>
<td>0.25</td>
</tr>
<tr>
<td>0.2</td>
<td>0.40</td>
<td>0.2</td>
<td>0.37</td>
</tr>
<tr>
<td>0.3</td>
<td>0.49</td>
<td>0.3</td>
<td>0.45</td>
</tr>
<tr>
<td>0.4</td>
<td>0.56</td>
<td>0.4</td>
<td>0.52</td>
</tr>
<tr>
<td>0.5</td>
<td>0.62</td>
<td>0.5</td>
<td>0.59</td>
</tr>
<tr>
<td>0.6</td>
<td>0.67</td>
<td>0.6</td>
<td>0.64</td>
</tr>
<tr>
<td>0.7</td>
<td>0.71</td>
<td>0.7</td>
<td>0.71</td>
</tr>
</tbody>
</table>
TABLE XII - ACTIVATION ENERGIES OF DESORPTION OF CESIUM FROM THE 0001, 10\bar{1}4, AND 10\bar{1}2 PLANES OF Rhenium versus average cesium concentration.

<table>
<thead>
<tr>
<th>Average coverage of adsorbed Cs (\bar{\eta}) atoms/m^2 x10^{18}</th>
<th>Desorption energy from the 0001 plane (E_{0001}) eV x10^{18}</th>
<th>Desorption energy from the 10\bar{1}4 plane (E_{10\bar{1}4}) eV x10^{18}</th>
<th>Desorption energy from the 10\bar{1}2 plane (E_{10\bar{1}2}) eV x10^{18}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>3.08</td>
<td>3.01</td>
<td>3.10</td>
</tr>
<tr>
<td>0.010</td>
<td>3.06</td>
<td>2.99</td>
<td>3.06</td>
</tr>
<tr>
<td>0.013</td>
<td>3.03</td>
<td>2.98</td>
<td>3.04</td>
</tr>
<tr>
<td>0.020</td>
<td>2.96</td>
<td>2.96</td>
<td>3.02</td>
</tr>
<tr>
<td>0.050</td>
<td>2.90</td>
<td>2.90</td>
<td>2.92</td>
</tr>
<tr>
<td>0.070</td>
<td>2.86</td>
<td>2.86</td>
<td>2.90</td>
</tr>
<tr>
<td>0.1</td>
<td>2.82</td>
<td>2.79</td>
<td>2.82</td>
</tr>
<tr>
<td>0.2</td>
<td>2.62</td>
<td>2.60</td>
<td>2.62</td>
</tr>
<tr>
<td>0.3</td>
<td>2.44</td>
<td>2.42</td>
<td>2.44</td>
</tr>
<tr>
<td>0.4</td>
<td>2.38</td>
<td>2.27</td>
<td>2.28</td>
</tr>
<tr>
<td>0.5</td>
<td>2.13</td>
<td>2.12</td>
<td>2.13</td>
</tr>
<tr>
<td>0.6</td>
<td>2.06</td>
<td>2.06</td>
<td>2.06</td>
</tr>
<tr>
<td>0.7</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
</tr>
</tbody>
</table>
gies as a function of \( \bar{n} \), considerably larger ones exist when the energies are correlated with actual individual plane concentrations. Thus Fig. 26 shows a difference in binding energy between the 10\( \bar{1} \)4 and 10\( \bar{1} \)2 planes of 0.2 eV at \( n \sim 0.1 \times 10^{18} \) atoms/m\(^2\). As expected the two higher work function planes have the greater binding energies and, within the limits of experimental error, these are equal for \( n < 0.2 \times 10^{18} \) atoms/m\(^2\).

A previously determined value of the terminal desorption\(^{54,58} \) of Cs from Re was 3.8 eV compared to the present extrapolated value of 3.1 eV. The present value is closer to the value of Cs on W.
Figure 26. Plots of binding energy versus coverage of Cs on various planes on Re.
EVALUATION OF THE METHODS USED TO OBTAIN ACTIVATION ENERGIES OF DESORPTION AND PREEXPONENTIALS OF DESORPTION

Desorption of Cs from field emitters occurs from a variety of crystal planes which exist on the emitter and its shank, consequently some discussion is warranted about the meaning of activation energies of desorption which are determined from total field emission current measurements. Schmidt and Gomer have discussed this problem and conclude that if an equilibrium distribution of adsorbate over the different regions of the emitter is maintained during desorption, then the observed activation energy of desorption will be biased toward the highest energy region. For the case of a substrate containing two regions of differing binding energy $H_1$ and $H_2$, these authors derived the following equation for rates of desorption $\frac{d \ln N_1}{dt}$, $\frac{d \ln N_2}{dt}$ from the two regions 1 and 2 containing $S_1$ and $S_2$ sites respectively; $N_1$ and $N_2$ are the corresponding amounts of adsorbate on the two regions.

$$\frac{-d \ln N_1}{dt} = \frac{-d \ln N_2}{dt} = \frac{\nu_1 \exp(-H_1/kT) + \nu_2 m'(S_2/S_1) \exp(-H_1/kT)}{1 + m (S_2/S_1) \exp(H_2 - H_1)/kT}$$

where $m'$ is the ratio of internal partition functions. A similar term to the one on the right also holds for ionic desorption in which case $H_1$ and $H_2$ are reduced by $I - \phi_1$ and $I - \phi_2$ respectively where $I$ is the adsorbate ionization potential and $\phi_1$ and $\phi_2$ represent the work functions of the regions 1 and 2.

When $\nu_1 \sim \nu_2 S_2 > S_1$ and $m' \sim 1$ we have

$$\frac{-d \ln N_1}{dt} = \frac{-d \ln N_2}{dt} = \frac{\nu \left( \exp(-H_1/kT) + \exp(-H_1/kT) \right)}{1 + \exp(H_2 - H_1)/kT}.$$
Suppose $T = 1000^\circ K$, $H_1 = 3.3 \text{ eV}$, $H_2 = 3.0 \text{ eV}$, these being typical values for two planes of W when Cs is adsorbed, then the resultant rates of desorption are reduced by only 3% below the value for a surface characterized by a single value of $H_1 = 3.3 \text{ eV}$. At higher adsorbate coverages, binding energies tend to converge, in which case, the rate of desorption is determined by an unambiguous desorption energy, applicable to binding on all planes.

The situation for desorption from substrates consisting of more than two planes is more complex, but in view of the above discussion it seems reasonable to expect that the desorption energy measured by total field emission techniques, $H$ will lie in the range:

$$\tilde{H} < H < H_{\text{max}}$$

where $\tilde{H}$ is the average desorption energy ($\tilde{H} = 1/a \left( H_1 + H_2 + \ldots + H_a \right)$) in which $H_1 \ldots H_a$ are individual plane desorption energies and $H_{\text{max}}$ is the greatest desorption energy of any plane. For Cs on W, $^{57}H_{\text{max}} - \tilde{H} \sim 0.3 \text{ eV}$, so that $H$ is unlikely to be more than 0.15 eV below $H_{\text{max}}$. Preliminary evidence indicates that this is true also for other substrates to which Cs is bound such as W/F, W/O and Re. The applicability of the assumption that equilibrium is maintained during desorption of Cs from the above substrates depends on the relation between the mean distance $\bar{x}$ which a Cs atom diffuses before evaporating and the linear dimensions, $l$, of the crystal planes participating in adsorption. If $\bar{x} >> l$, then equilibrium is maintained during desorption. Gomer and Schmidt$^{50}$ estimated that this relation held under all conditions at the desorption temperature for K on W. Because
of the similarity between the adsorption and diffusion behavior of K on W and Cs on Re and W, it is felt that \( \tilde{x} \gg \xi \) also holds for the latter systems at the desorption temperature. \( \tilde{x} \) is given by:

\[
\tilde{x} = a' \exp\left(\frac{H - H_{\text{diff}}}{2kT}\right)
\]

(34)

where \( a' \sim 3 \, \text{Å} \) and \( H_{\text{diff}} \) is the diffusion energy. For the coadsorbed systems \( H - H_{\text{diff}} \) is somewhat less than for clean W at \( n \sim 1.5 \times 10^{18} \) atoms/m\(^2\) and this may be the reason the decline of the \( H_2/n \) curve below the clean W curves in the coverage range \( n > 1.0 \times 10^{18} \) atoms/m\(^2\).

The preexponential of desorption \( \nu \) is given by\(^59\)

\[
\nu = \frac{kT}{h j_\nu}
\]

(35)

where \( h \) is Planck's constant and \( j_\nu \) is the partition function given by:

\[
j_\nu = (1 - \exp[-h \nu/kT])^{-1}
\]

(36)

where \( \nu \) is the vibrational frequency of the excited atom. For Cs on the substrates discussed in this report, \( h \nu \gg kT \) and in this case we have

\[
\nu = \frac{kT}{h}.
\]

(37)

The fact that \( \nu \) is dependent on \( T \) results in only a 4% variation in \( \log \nu \) over the temperature required for Cs desorption so that variation of \( \log \nu \) with \( T \) may be neglected as may variation with crystal plane structure or composition. This latter fact enables \( \log \nu \) to be filtered out of Eq. (32) and requires evaluation of a term \( \log\left[1 + m'(S_2/S_1)\right] \) in order to estimate \( \nu \).
A reasonable assumption is that \( m' = 1 \) for all planes so that \( \log[1 + m'(S_2/S_1)] \longrightarrow \log(1 + S_2/S_1) \) which if \( S_2/S_1 \approx 4 \) gives \( \ln(1 + S_2/S_1) \approx 0.7 \). Hence it can be seen that average desorption measurements from a variety of planes can lead in principle to errors in the experimental evaluation of \( \nu \); however \( \nu \) determined from average measurements on polycrystalline samples does not depart appreciably from expected values based on \( \nu = kT/h \).

**Average Work Functions from Total Field Emission Current Measurements**

For field electron emission from a variety of planes, the relation between emitted current \( I \) and voltage \( V \) is given by:

\[
I/V^2 = \sum a_i \exp(-b'_i \theta_i^{3/2}/V)
\]

where \( a_i, b'_i \) are constants applicable to plane \( i \).

A measured average work function \( \langle \theta \rangle \) is experimentally determined from the slope of plots of \( \log I/V^2 \) versus \( 1/V \). Thus:

\[
d \ln(I/V^2)/d(1/V) = \langle b'_i \theta_i^{3/2} \rangle
\]

from which may be derived:

\[
\langle \theta^{3/2} \rangle = \sum f_i (b'_i / \langle b'_i \rangle) \theta_i^{3/2}
\]

where \( f_i \) is the fraction of the total current carried by the \( i \)th emitting region. Since \( f_i \) depends on \( V \), \( \langle \theta \rangle \) also will vary with \( V \), however, the curvature of \( \ln (I/V^2) \) is negligible over the voltage range usually studied. Eq. (40) indi-
cates that the measured average work function is heavily weighted in favor of the lowest work function area (most highly electron emitting) of the emitter.

Two other uncertainties attend interpretation of average field emission work functions: these relate to the electron emission anisotropies before and after adsorption and to the possibility of local change in $b'$ as a result of substrate rearrangement on some planes of the emitter. For the alkali metals electronegative adsorbates, the electron emission anisotropy in the coverage range $0 < n < n_{\text{min}}$ (where $n_{\text{min}}$ is the Cs coverage corresponding to the work function minimum) is different from that of the clean emitter. In this case, the reference work functions of the clean emitter are much higher than the measured average of the clean emitter. When oxygenated W emitters are heated, oxide build-up occurs on the 111 plane to such an extent that at high enough temperatures these become the predominant emitting planes. In this case, a significant decrease in $b'$ occurs relative to the clean value. However, only absolute measurements of field emission work function can yield information about the extent of $b'$ change.
CONCLUSIONS

This report deals with absolute and relative work function measurements at different temperatures on various single planes of W, Nb, Ni, Cu, Re; included also is information on the desorption constants of Cs from O and F covered W and from Re field emitters.

The field emission retarding potential technique, used in this work offers an exceptionally accurate technique for measuring work functions of macroscopic crystals. Provided that the probing electron beam emerges from a crystal direction which is free from special energy band effects, the interpretation of the experimental data is unambiguous. The field emission probe technique in which the current voltage characteristics of a single plane are examined and thermionic techniques are subject to uncertainty when certain crystal planes such as (0001) Re and (110) W are investigated. In these cases it seems reasonable to suppose that energy band artifacts interfere with and result in anomalously high work function values for these two planes. For other planes, work function values do not appear to depend on method of measurement.

Temperature coefficients of work function are such that extrapolated work functions tend to converge at high temperatures $T_m$. Thermodynamic arguments identify $T_m$ with the melting point of the metal and experimental results tend to confirm this idea except for (0001) Re and (110) W.

The activation energies of desorption $H$ of Cs neutrals from W/O and W/F field emitter substrates are very similar. In both cases, $H$ rises above
the clean W value for Cs coverages less than \( \sim 1 \times 10^{18} \) atoms/m\(^2\). The terminal energy for Cs neutral desorption from W/O is 4.1 ± 0.3 eV while that from W/F is 3.9 ± 0.3 eV; no significant differences in H occurred. Terminal desorption of Cs neutrals is accompanied by concomitant desorption of F from W/F substrates but not O from W/O substrates.

The close packed planes of Re, (0001) and (10\( \bar{1} \)2), bind Cs more strongly than the (10\( \bar{1} \)4) plane and low coverage, the difference between H (0001) and H (10\( \bar{1} \)2) on one hand and (10\( \bar{1} \)4) on the other, amount to about 0.2 eV. The terminal desorption energy of Cs from Re was determined to be 3.1 eV.
REFERENCES


APPENDIX

LIST OF SYMBOLS USED

\( A \) \hspace{1cm} \text{preexponential of Fowler-Nordheim equation}

\( A_R \) \hspace{1cm} \text{Richardson constant}

\( a \) \hspace{1cm} \text{integer}

\( a' \) \hspace{1cm} \text{difference between desorption and diffusion energies}

\( a_1 \) \hspace{1cm} \text{preexponential of field emission current sum}

\( b \) \hspace{1cm} \text{constant in linear equation}

\( b_1' \) \hspace{1cm} \text{Fowler-Nordheim field emission exponential constant}

\( C \) \hspace{1cm} \text{constant in linear equation}

\( C(d_O, \sigma) \) \hspace{1cm} \text{a function of adsorbate density and size which relates the contact potential to that existing at an actual site}

\( d \) \hspace{1cm} \text{energy distribution parameter}

\( d_0 \) \hspace{1cm} \text{distance from the center of charge of an adsorbed ion to the surface}

\( E \) \hspace{1cm} \text{electron energy}

\( E_f \) \hspace{1cm} \text{electron energy at Fermi level}

\( \Delta E \) \hspace{1cm} \text{energy resolution}

\( F \) \hspace{1cm} \text{electric field}

\( F_1 \) \hspace{1cm} \text{Helmholtz activation energy of desorption of cesium from plane 1}

\( F_2 \) \hspace{1cm} \text{Helmholtz activation energy of desorption of cesium from plane 2}

\( f_i \) \hspace{1cm} \text{the fraction of total field emission current carried by i th emitting region}

\( g \) \hspace{1cm} \text{differential of binding energy with respect to surface coverage}
\( g' \) charge per adatom

\( H \) activation enthalpy of desorption

\( \bar{H} \) average activation enthalpy of desorption

\( H_1 \) activation enthalpy of desorption from plane 1

\( H_2 \) activation enthalpy of desorption from plane 2

\( H_{\text{diff}} \) activation enthalpy of diffusion

\( I \) field emission current

\( I_0 \) total collected current

\( I_0' \) reference field emission current

\( j \) current density

\( j_0 \) total emitted current density

\( j_V \) partition function

\( k \) Boltzmann constant

\( l \) linear dimension of field emitter

\( m' \) ratio of partition functions

\( m \) slope of Fowler-Nordheim equation

\( m_a \) value of Fowler-Nordheim slope corresponding to emitter with adsorbate on it

\( m_c \) corresponding value of \( m \) for clean emitter

\( \bar{n} \) average adsorbate coverage (atoms/m\(^2\))

\( n \) fractional bond

\( n_a \) number of nearest neighbors

\( n_b \) number of next nearest neighbors of surface atoms

\( N_a \) number of nearest neighbors on surface
\( N_b \)  
number of next nearest neighbors of surface atoms

\( N_1 \)  
number of adsorbate particles on plane 1

\( N_2 \)  
number of adsorbate particles on plane 2

\( n_o \)  
adsorbate coverage when \( \Theta = 1 \), i.e. at monolayer coverage

\( n_1 \)  
adsorbate coverage on plane 1

\( n_2 \)  
adsorbate coverage on plane 2

\( n_i \)  
adsorbate coverage on plane i

\( n_{110} \)  
adsorbate coverage on 110 plane of tungsten

\( n_{0001} \)  
adsorbate coverage on 0001 plane of rhenium

\( P \)  
pressure

\( R \)  
distance between two surface atoms

\( R_a \)  
distance between nearest neighbor atoms

\( R_b \)  
distance between next nearest neighbor atoms

\( r_s \)  
bonding energy of surface atom

\( r_m \)  
effective atom size (atomic radius)

\( S \)  
slope of Arrhenius plot

\( S_1 \)  
number of adsorbate sites on plane 1

\( S_2 \)  
number of adsorbate sites on plane 2

\( T \)  
temperature

\( T_L \)  
temperature for which adsorbate equilibrium occurs in ~ 1000 sec.

\( T_H \)  
temperature which corresponds to frozen adsorbate distribution

\( t \)  
time

\( t(y) \)  
tabulated function of \( F \) and \( \phi \)
emitter voltage
lens voltage
anode voltage
collector voltage
variable in linear equation
average distance traveled by migrating atom before it desolves
variable in linear equation
temperature correction term to slope of Fowler-Nordheim equation
electron energy relative to Fermi
angle between Cs source and normal to region i being probed
average value of emitter field emission factor which relates field F to voltage V : \( F = \beta V \)
relative surface coverage on plane i
relative surface coverage for whole emitter
average work function of emitter covered with adsorbate
average work function of clean emitter
collector work function
work function of plane i
average emitter work function
Richardson work function
work function temperature coefficient
preexponential desorption factor
preexponential desorption factor for plane 1
\( \nu_2 \)  
preexponential desorption factor for plane 2

\( \mu \)  
dipole moment

\( T_c \)  
time constant for cooling the emitter