A STUDY OF SURFACE REACTIONS BY
FIELD EMISSION MICROSCOPY

by

John Read Arthur, Jr.

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa
1961
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>FIELD EMISSION MICROSCOPY</strong></td>
<td>3</td>
</tr>
<tr>
<td><strong>FLASH FILAMENT DESORPTION</strong></td>
<td>16</td>
</tr>
<tr>
<td><strong>EXPERIMENTAL PROCEDURES</strong></td>
<td>22</td>
</tr>
<tr>
<td>Introduction</td>
<td>22</td>
</tr>
<tr>
<td>Ultra-high Vacuum Techniques</td>
<td>23</td>
</tr>
<tr>
<td>Construction of Field Emission Microscopes</td>
<td>27</td>
</tr>
<tr>
<td>Temperature Control</td>
<td>32</td>
</tr>
<tr>
<td>Low-temperature Experiments</td>
<td>41</td>
</tr>
<tr>
<td>Flash Filament Experiments</td>
<td>45</td>
</tr>
<tr>
<td><strong>RESULTS</strong></td>
<td>48</td>
</tr>
<tr>
<td>Field Emission from Clean Iridium</td>
<td>48</td>
</tr>
<tr>
<td>Field Emission from Covered Iridium</td>
<td>59</td>
</tr>
<tr>
<td>Adsorption of ethylene</td>
<td>59</td>
</tr>
<tr>
<td>Adsorption of acetylene</td>
<td>81</td>
</tr>
<tr>
<td>Adsorption of ethane</td>
<td>92</td>
</tr>
<tr>
<td>Adsorption of hydrogen</td>
<td>92</td>
</tr>
<tr>
<td>Kinetic studies</td>
<td>94</td>
</tr>
<tr>
<td>Flash Desorption Experiments</td>
<td>104</td>
</tr>
<tr>
<td>Desorption of hydrogen</td>
<td>104</td>
</tr>
<tr>
<td>Desorption of ethylene</td>
<td>114</td>
</tr>
<tr>
<td><strong>DISCUSSION</strong></td>
<td>117</td>
</tr>
<tr>
<td>Adsorption of Hydrogen</td>
<td>118</td>
</tr>
<tr>
<td>Adsorption of Ethane</td>
<td>124</td>
</tr>
<tr>
<td>Adsorption of Ethylene</td>
<td>125</td>
</tr>
<tr>
<td>Adsorption and initial dehydrogenation</td>
<td>126</td>
</tr>
<tr>
<td>Final dehydrogenation of ethylene</td>
<td>130</td>
</tr>
<tr>
<td>Adsorption of ethylene on other metals</td>
<td>135</td>
</tr>
<tr>
<td>Adsorption of Acetylene</td>
<td>138</td>
</tr>
<tr>
<td>Applications to Catalysis</td>
<td>140</td>
</tr>
</tbody>
</table>
INTRODUCTION

The reactions between hydrogen and unsaturated hydrocarbons in the presence of metal surfaces are some of the most useful and least understood processes in chemistry. A vast amount of effort has been spent in trying to understand these reactions, yet the mechanisms remain largely unknown.

This is not surprising when one considers the difficulties inherent in studies of surface reactions. A prime difficulty is the small number of atoms in the surface. A square centimeter of surface has about $10^{15}$ atoms exposed, or $10^{-8}$ moles. Furthermore, impurity concentrations of as little as 1%, or $10^{-10}$ moles, can cause marked changes in surface properties. Thus for any fundamental study of surface reactions one must begin with a clean surface. Moreover, it must be possible to characterize this surface and preserve its cleanliness until the reaction begins. The difficulty in preservation may be assessed from the fact that even in a vacuum as high as $10^{-6}$ mm Hg enough gas molecules strike the surface every second to form a monolayer. Clearly, pressures several orders of magnitude lower are necessary to preserve the clean surface for even minutes. Since the technology for performing these tasks has only become available within the last ten years it is not surprising that progress has been slow.

A powerful tool for studying metal surfaces is the field emission electron microscope. The electron emission from a
metal surface serves as a very sensitive indication of the surface purity. The field emission microscope (FEM) displays the electron emission from individual planes of a metal crystal, thus providing information about the location as well as amount of surface impurity. Moreover, the microscope emitter can be operated in a vacuum so good that clean surfaces can be maintained for hours or even days. If the emitter material is a metal whose oxides are volatile or decompose below the melting point of the metal, the emitter surface can be cleaned simply by heating in a very good vacuum. Thus experiments can be conducted in which a clean surface is prepared and characterized, then allowed to adsorb a known gas. From the electron emission pattern the progress of the adsorption can be observed on the various crystal planes; by heating the emitter, surface migration and desorption processes can be observed. From these observations the kinetics of reactions on clean surfaces can be followed. With a knowledge of rates, kinetic orders, and activation energies, one may ultimately be able to determine reaction mechanisms and evaluate the role of the surface in heterogeneous catalysis. This work is an attempt to apply field emission microscopy in fundamental studies of adsorption and surface reactions of hydrocarbons on iridium.
FIELD EMISSION MICROSCOPY

Field emission is a phenomenon involving the emission of electrons from a solid as a result of the application of a strong electric field. The temperature of the emitting material has very little effect on the emission in contrast to thermionic emission which only occurs at elevated temperatures.

The theory of field emission from metals has been developed by Fowler and Nordheim (1) using the free electron model for the behavior of electrons in a metal. In this model, the metal is regarded as a potential well in which are placed the conduction electrons considered as non-interacting particles. Since the electrons obey Fermi-Dirac statistics only two electrons (with opposite spin) are allowed in each energy level. At absolute zero the electrons exactly fill the available levels up to an energy $\mu_0$, the Fermi energy. ($\mu_0$ is measured from the bottom of the well. See Figure 1.) At temperatures above zero, some electrons are thermally excited above the Fermi level leaving vacancies below; the Fermi level then becomes that energy level for which the probability of being filled is one-half. The thermal excitation is of the order of $kT$, which at 300 °K is 0.03 electron volts. Since $\mu_0$ amounts to several electron volts the most energetic electrons in the metal still have energies very close to $\mu_0$ at normal temperatures.
We will define the amount of work required to remove an electron from the Fermi level to an infinite distance away from a finite metal surface in the absence of any external fields as the absolute work function $\phi_a$. This is simply the difference between the depth of the potential well and the Fermi energy, and in principle can be calculated if the electronic wave functions in the metal are known (2). $\phi_a$ as defined depends only on the bulk properties of the metal and not on crystallographic orientation or surface condition. On the other hand, the work necessary to remove an electron to a distance from the metal which is small compared to the dimensions of the surface will depend markedly on surface effects. When material is adsorbed on the surface of a metal, charge transfer results in the formation of a dipole layer at the surface. Even in the absence of adsorption a dipole layer exists since the metal is not made up of neutral atoms but rather of positive ion cores and a negative electron gas. The moment of the dipoles depends on crystallographic orientation since the positive cores protrude more on the rough (high index) crystal planes. The potential due to these dipole layers is very nearly equivalent to that of a continuous electrical double layer,

$$V(x) = n_o \tau \omega$$  \hspace{1cm} (1)

where $\tau$ is the unit dipole moment, $n_o$ the number of dipoles per unit area and $\omega$ the solid angle subtended by the surface.
at the point $x$ (3).

To remove an electron from the Fermi level to a distance $x$ from the surface will then require an amount of work $\Phi_a$ to remove the electron to infinity plus an amount $eV(x)$ to bring the electron back to the point $x$; i.e.,

$$\phi(x) = \Phi_a + eV(x) \quad (2)$$

If $x$ is small compared to the surface dimensions, $\omega = 2\pi$ and thus

$$\phi = \Phi_a + 2\pi e n_0 \tau \quad (3)$$

Experimental methods for measuring work functions all depend on the passage of electrons over a potential energy barrier which is located close to the surface (4) and thus measure $\phi$ and not $\Phi_a$. Therefore we shall henceforth call $\phi$ the work function.

So far it has been implied that the surface potential barrier is a step-function such as Fowler and Nordheim originally assumed. A more realistic assumption is a classical image potential for the surface barrier. A charged particle induces an opposite charge on a conducting surface and is thus attracted to the surface. Then the potential energy of an electron a distance $x$ away from an infinite planar conducting surface is (3),

$$E(x) = \frac{-e^2}{4x} \quad (4)$$

Such a potential function is not likely to be valid at extremely short distances from the surface but is a fairly good
approximation at distances greater than a few angstrom units.

Figure 1 shows a potential energy diagram for tungsten. Figure 1b shows the effect of an applied electric field of $3 \times 10^7$ v/cm. Also indicated is the change in work function caused by the adsorption of $5 \times 10^{14}$ atoms/cm$^2$ with a metal-adatom bond moment of 1.1 debyes.

From a classical viewpoint the only electrons which can leave the metal are those with a kinetic energy greater than $\phi$. This results in thermionic emission. The emission current follows the Richardson equation

$$J = A T^2 \exp \left[ -\frac{\phi}{kT} \right]$$  \hspace{1cm} (5)

It is readily shown that an applied field $F$ lowers the work function by an amount

$$\Delta \phi = e \sqrt{eF}$$  \hspace{1cm} (6)

as illustrated in Figure 1b.

Schottky (5) generalized the Richardson equation to include this effect and suggested that field emission might occur when the field was high enough to reduce the effective work function to zero. However, this model implied a strong temperature dependence of field emission current which was not observed, and required higher fields than were found necessary.

The present theory of field emission is based on the work of Fowler and Nordheim (1) who showed that emission could occur by quantum-mechanical tunneling. Tunneling permits
Figure 1a. Potential energy diagram of a metal surface

Figure 1b. Potential energy diagram of a metal surface with an applied electrostatic field
DISTANCE FROM SURFACE

METAL

VACUUM

POTENTIAL OF DIPOLE LAYER

APPLIED FIELD OF $3 \times 10^7$ V/Cm

POTENTIAL BARRIER FOR METAL WITH DIPOLE LAYER

POTENTIAL BARRIER FOR CLEAN METAL

IMAGE POTENTIAL
electrons which do not have enough kinetic energy to get over the surface barrier to leak through the barrier. The Heisenberg uncertainty principle states that
\[ \Delta p \cdot \Delta x \simeq \hbar \]  
(7)

Since the electrons in the metal do not have enough kinetic energy to surmount the barrier,
\[ \Delta p = (2m \Delta E_k)^{\frac{1}{2}} < (2m\varphi)^{\frac{1}{2}} \]  
(8)

If \( \Delta x \) is of the order of the thickness of the surface barrier, emission can result since an electron has a finite probability for being on either side of the barrier. Now from Figure 1b the thickness is
\[ x = \frac{\varphi}{Fe} \]  
(9)

since the barrier is approximately triangular. Therefore
\[ \Delta p \cdot \Delta x = (2m\varphi)^{\frac{1}{2}} \cdot \frac{\varphi}{Fe} = \frac{\hbar}{2\pi} \]  
(10)

or
\[ \left( \frac{2m}{\hbar^2 e^2} \right)^{\frac{1}{2}} \frac{\varphi^{3/2}}{F} = 5.1 \times 10^7 \frac{\varphi^{3/2}}{F} \simeq 1 \]  
(11)

when \( \varphi \) is in electron volts and \( F \) in volts/cm. This is approximately the condition for emission. (See Equation 12.)

The more rigorous treatment by Fowler and Nordheim considers the product of the probability that electrons of a given energy can penetrate the barrier and the number of such electrons reaching the barrier per unit time. This product integrated over all energies gives the current density. The Fowler-Nordheim equation is (7)
\[ J = 6.2 \times 10^{-6} \left( \frac{\mu/\varphi}{\mu + \varphi} \right) \frac{F^2}{\varphi} \exp \left[ -6.8 \times 10^7 \frac{\varphi^{3/2}}{F} \right] \text{amp/cm}^2 \]  

(12)

for energies in electron volts and \( F \) in volts/cm. Nordheim (6) modified this equation to include an image potential barrier. Certain refinements in his treatment have been made, leading to the present form (8)

\[ J = (1.54 \times 10^{-6} \frac{E^2}{t^2(y)\varphi}) \exp \left[ -6.83 \times 10^7 \frac{\varphi^{3/2} f(y)}{F} \right] \text{amps/cm}^2 \]  

(13)

\( t(y) \) and \( f(y) \) are functions of the variable

\[ y = 3.79 \times 10^{-4} \frac{E^{1/2}}{\varphi} \]  

(14)

which have been tabulated (8, 9). A table of values of the logarithm of current density at various fields and work functions has been calculated by Dolan (10) with \( t(y) \) set equal to unity. This is a frequently used simplification since \( 0.8 < \frac{1}{t^2} < 1 \) for the range of \( y \) that is of interest.

A considerable amount of effort has been spent in attempts to verify the Fowler-Nordheim equation experimentally. In all cases the agreement between theory and experiment has been excellent. More complete discussions of these experiments and the history of field emission in general are given in some of the numerous review articles on field emission (7, 8, 11).

The field emission microscope displays the field emission current from the individual planes of a small metal crystal
upon a fluorescent screen. The emitter is a fine wire which has been etched to a sharp point. On a microscopic scale the end of the point is an almost hemispherical, single crystal with a radius of 1000 to 5000 Å. Electrons emitted by the crystal travel on paths nearly normal to the surface and, upon striking the screen, furnish a greatly magnified map of the variation in work function over the surface. Since the work function of a surface is quite sensitive to adsorbed material, the FEM provides a rapid indication of the amount and location of surface impurities. Thus the FEM is a valuable tool for characterizing the emission properties of clean metal surfaces.

The FEM is also valuable for studying adsorption on clean metal surfaces. Since the end of the emitter is nearly spherical, a large number of crystal planes are exposed. By observing emission patterns during adsorption and desorption it is possible to determine how the relative rates of these processes depend on crystal face. The direction of bond moment is indicated by the sign of the work function change; the fractional coverage is given by the magnitude. Kinetic information can be obtained by measuring the rates of work function change.

However, the FEM is still relatively unexploited in adsorption studies. The work which has been done is well summarized in review articles by Becker (12, 13) and Gomer (14). The results of such work have considerably altered our
understanding of adsorption phenomena.

At the same time it is only fair to point out that the FEM has definite limitations in adsorption studies. The quantity which is directly measurable is the total emission current and its dependence on the applied voltage. Qualitative observations of the variation in current density over the surface can be made, but in general it is difficult to measure this variation quantitatively. From the current-voltage characteristics of an emitter it is possible to obtain information about an average work function of the surface; however this quantity must be carefully defined.

The Fowler-Nordheim equation for a surface of work function \( \varphi \) and area \( A \) can be written

\[
I = JA = a V^2 \exp \left[ -b \frac{3/2}{V} \right]
\]

(15)

where \( V \) is the voltage applied to the anode and is proportional to the field,

\[
F = \beta V
\]

(16)

Then if \( \log I/V^2 \) is plotted against \( 1/V \), the result should be a straight line with slope \( -b \varphi^{3/2} \). If \( S_o = \left[ -b \varphi_o^{3/2} \right] \) is the slope of such a plot for a clean surface and \( S = \left[ -b \varphi^{3/2} \right] \) the slope for a surface covered with adsorbed gas, then

\[
\varphi = \left[ \frac{S}{S_o} \right]^{2/3} \varphi_o
\]

(17)

Thus if the work function for the clean surface is known, the
change upon adsorption can be obtained from the slopes of the
Fowler-Nordheim plots. This treatment assumes that the factor
b remains constant. From Equation 14 it follows that
\[ b = 6.87 \times 10^7 \times \frac{f(y)}{\beta} \]  
(18)
where \( \beta \) is the "sharpness factor" from Equation 16. Since
\( f(y) \) is a very slowly varying function of \( \varphi \), \( b \) is nearly un-
changed by adsorption.

However, the surface of a real field emitter is "patchy", i.e., it consists of areas of different work function. The
measured current is then the sum of the individual patch
currents so that
\[ \frac{I}{V^2} = \sum_i \frac{I_i}{V^2} = \sum_i a_i \exp \left[ -b_i \frac{\varphi_i^{3/2}}{V} \right] \]  
(19)
We define an average work function \( \overline{\varphi} \) such that
\[ \frac{I}{V^2} = \bar{a} \exp \left[ -\overline{\varphi}^{3/2}/V \right] \]  
(20)
Now \([-b \overline{\varphi}^{3/2}\)] will be the slope of the F-N plot using the
total current. It can easily be shown that
\[ \overline{\varphi}^{3/2} = \sum_i \frac{I_i}{I} \frac{b_i}{b} \varphi_i^{3/2} \]  
(21)
Thus the apparent work function determined from a patchy sur-
face is an average value which is heavily weighted in favor of
the low work function planes. It can be calculated that a
surface containing two patches of equal area with \( \varphi \)'s of 4.5
and 5.0 e.v. have a \( \overline{\varphi} \) of 4.51 e.v. at a field of \( 3 \times 10^7 \) v/cm.

From Equation 21, it is evident that changes in \( \overline{\varphi} \) with
adsorption must be interpreted carefully. It is often assumed (see Equation 3) that

$$\theta = \frac{\Delta \phi}{\Delta \varphi_{\text{max}}} = \frac{n}{n_0}$$

where $\theta$ is the fractional coverage and $\Delta \varphi_{\text{max}}$ is the change in $\varphi$ when a monolayer has been adsorbed. This will be strictly true for $\Delta \bar{\varphi}$ only when $\Delta \varphi_i$ is the same for all the patches. In general, adsorption and desorption processes have somewhat different rates on different crystal planes. However, the areas which usually are the most active are the atomically rough, high index planes. These are the planes which have the lowest work functions and thus contribute predominantly to $\bar{\varphi}$. Thus changes in $\bar{\varphi}$ will be indicative of the coverage on these active planes.

For Equation 22 to be valid, it is also necessary that the dipole moment per adatom remain constant with coverage. This is generally assumed to be the case; however there is very little experimental evidence to support this assumption. One mechanism by which the bond moment might change is the mutual depolarization of the individual dipoles. Since dipolar forces are weak and decrease rapidly with distance, such depolarization is likely only at very high coverage with strong dipoles, e.g., cesium on tungsten.

Thus it can be seen that the information furnished by the FEM is not unambiguous, and interpretations must be made.
carefully. However, the FEM can furnish a great deal of information about adsorption and desorption on clean metal surfaces. A very extensive discussion of the theory and practice of field emission microscopy is presented in a recent book by Gomer (15). This is the most complete single source and should be the starting point for all desiring more information on the subject.
FLASH FILAMENT DESORPTION

One limitation of the field emission microscope is its inability to determine how much material has been adsorbed on the surface of the emitter. Relative coverage can be inferred (Equation 21) but this gives little indication of the total number of molecules adsorbed. The change in work function gives a measure of the surface dipole moment per unit area, $n_0 \tau$, but since the unit dipole moment $\tau$ cannot be predicted a priori, $n_0$ is still undetermined.

A simple but effective method for determining the amount of material adsorbed on a filament is flash filament desorption. If a wire filament is quickly heated to a very high temperature in a closed system at a low pressure, the rise in pressure in the system is a direct indication of the total number of molecules which have desorbed from the filament.

$$n_0 = \frac{V \Delta P}{kT \Delta A}$$

where $n_0$ is the number of adsorbed molecules per cm$^2$, $V$ is the volume of the system and $A$ the surface area of the filament.

This technique was first applied by Becker (12, 16) to the adsorption of nitrogen on tungsten. Besides measuring the amount of adsorbed nitrogen, Becker was able to evaluate the sticking coefficient, i.e., the probability that a molecule striking the surface will become chemisorbed. This was done by recording the pressure in a closed system as a function of
the time after cleaning the surface (by flashing). The number of molecules $N$ striking unit area of surface per second is given by kinetic theory as

$$N = \frac{P}{\sqrt{2\pi mkT}} = \frac{3.5 \times 10^{22}}{\sqrt{MT}} P$$

(24)

when $P$ is in mm Hg and $M$ is the molecular weight. The rate at which the surface concentration increases is

$$\frac{dn}{dt} = \frac{3.5 \times 10^{22}}{\sqrt{MT}} Pa$$

(25)

where $\alpha$ is the sticking coefficient. From filament flashes after various adsorption periods

$$\frac{dn}{dt} = \frac{V}{kTA} \frac{d\Delta P}{dt}$$

(26)

Thus $\alpha$ can be evaluated from

$$\alpha = \frac{\sqrt{MT}}{3.5 \times 10^{22}} \frac{V}{kTA} \frac{1}{P} \frac{d\Delta P}{dt}$$

(27)

The measurements of sticking coefficients on tungsten have shown that the adsorption process is somewhat more complex than had previously been realized. The coefficients are less than unity for all gases except cesium and show widely varying behavior with coverage. Most gases show two ranges of $n_o$ over which $\alpha$ is nearly constant. These ranges correspond roughly to a 1:2 and 1:1 ratio of molecules to surface tungsten atoms. Becker proposed that incoming molecules are first physically adsorbed on the surface and can migrate freely until they encounter adsorption sites. While in this pre-
adsorbed state molecules can desorb. The ratio of the rates of these processes determines \( \alpha \). Kisliuk (17, 18) has derived quantitative values for \( \alpha \) using a similar model. His results agree with experiment at low coverage but do not explain the behavior of \( \alpha \) as the surface becomes saturated.

In a recent series of papers (19, 20, 21, 22, 23) Ehrlich and Hickmott have shown that activation energies for desorption can be obtained by analysis of the rate of gas evolution during a flash. The desorption rate can be followed by monitoring the pressure rise during the flash using a fast response ion gauge and recorder. If a constant voltage is applied to a filament, the rate of temperature rise is nearly linear and over a limited range the filament temperature may be approximated by

\[
\frac{1}{T} = a + bt
\]  

(28)

The rate of pressure change in an evacuated system is

\[
\frac{dP}{dt} = \frac{kT}{V} F - \frac{S}{V} P
\]  

(29)

where \( F \) is the number of molecules being released into the system per second and \( S \) is the pumping speed in liters per second of all gas sinks. We shall isolate the system from pumps and external gas sources so that \( S \) is very small and \( F \) arises solely from desorption. We shall assume that the isothermal rate of gas evolution from a filament is given by the Polanyi-Wigner equation,
\[ F = -A \frac{dn}{dt} = Av^n \exp \left[ \frac{-AH}{RT} \right] \]  

(30)

where \( n \) is the number of molecules adsorbed per \( \text{cm}^2 \), \( A \) is the area of the wire, \( v \) is the frequency factor and \( x \) is the kinetic order of the reaction. From Equation 28, it follows that

\[ F = Av^n \exp \left[ \frac{-AH}{R} \right] \exp \left[ \frac{-AH}{RT} t \right] \]  

(31)

or

\[ -\frac{dn}{dt} = v' n^x e^{\alpha t} \]  

(32)

where

\[ v' = v \exp \left[ \frac{-AH}{R} \right], \]  

\[ \alpha = \frac{-AHb}{R} \]  

(33)  

(34)

Integrating, from \( t_0 \) to \( t \),

\[ \frac{v'}{\alpha} \left[ e^{\alpha t} - e^{\alpha t_0} \right] = x(t) = \begin{cases} \ln \frac{n_0}{n} & \text{if } x = 1 \\ \frac{n_0 - n}{n_0} & \text{if } x = 2 \end{cases} \]  

(35)

where \( n_0 \) is the initial number of molecules on the surface per \( \text{cm}^2 \) and \( t_0 \) is the time at which desorption begins. By limiting the range of integration to that time interval \( t_0 \) to \( t \) during which desorption is occurring, the range over which Equation 28 is assumed valid is reduced. Now

\[ n_0 - n = \frac{v}{kTA} \Delta P \]

and

\[ n_0 = \frac{V}{kTA} \Delta P_m \]  

(36)
where $\Delta P$ is the instantaneous pressure rise and $\Delta P_m$ is the final pressure rise in the system. Thus

$$X(t) = \begin{cases} \ln \frac{\Delta P_m}{\Delta P_m - \Delta P}, & x = 1 \\ \frac{\Delta P}{\Delta P_m(\Delta P_m - \Delta P)}, & x = 2 \end{cases}$$

(37)

Now since $t$ and $T$ are related by Equation 28

$$X(t) = X(T) = \frac{\nu R}{R} \left( e^{\frac{-\Delta H}{RT}} - e^{\frac{-\Delta H}{RT_0}} \right)$$

(38)

Then

$$\frac{d \ln X(T)}{d \left( \frac{1}{T} \right)} = \frac{-\Delta H}{R} \left\{ \frac{1}{1 - \exp \left[\frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right]} \right\}$$

(39)

Except for $T$ very close to $T_0$

$$\exp \left[ \frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \ll 1$$

(40)

and can be neglected. Thus a logarithmic plot against $1/T$ of

$$\ln \left( \frac{\Delta P_m}{\Delta P_m - \Delta P} \right)$$

in the case of first order desorption or

$$\frac{\Delta P}{\Delta P_m - \Delta P}$$

for a second order desorption is a straight line with slope $\frac{-\Delta H}{R}$. The kinetic order is indicated by which plot is linear.

It should be emphasized that the analysis presented above is based on the assumptions that $\Delta H$ and $\nu$ are independent of $n$. Experimentally it is found that $\nu$ and $\Delta H$ are fairly constant at low coverages. For nitrogen on tungsten (21) $\Delta H$ is constant at all coverages while for hydrogen on tungsten (20) $\Delta H$ is constant up to $n_o = 30 \times 10^{12}$ molecules/cm$^2$ but decreases
at higher concentrations.

Continuous recording of the pressure rise during a flash has disclosed some remarkable complexity in adsorption. Ehrlich (21) has observed that nitrogen desorbs from tungsten in three stages, indicating the existence of three binding states. He believes that the nitrogen with the lowest desorption activation energy is adsorbed as molecules while the more tightly bound forms are adsorbed as atoms. Carbon monoxide shows a very complex desorption spectrum with some four states resolvable (22, 24). Hydrogen adsorbed on tungsten at 77 °K shows two binding states (20). In most cases only one of the binding states can be treated by the analysis above; the others are usually present in relatively small amounts or are not adequately resolved. However, estimates of the activation energy are easily made from the temperature range over which desorption occurs.

Thus flash filament desorption can be used to determine the kinetics of adsorption and desorption processes and the quantity of material which is adsorbed. This information can be used to supplement the surface kinetic data provided by the field emission microscope.
EXPERIMENTAL PROCEDURES

Introduction

In order to gain a fundamental understanding of the interaction of unsaturated hydrocarbons with catalyst metal surfaces, studies of the adsorption of ethane, ethylene, acetylene and hydrogen on iridium were undertaken using field emission microscopy and flash filament desorption. The most extensive work was carried out with ethylene since it is the simplest molecule containing an unsaturated carbon-carbon bond. Supplementary work was done with ethane and acetylene to observe the effects of all stages of hydrogenation upon adsorption. Because of its unquestionable importance in surface hydrogenation and dehydrogenation reactions, hydrogen was also studied. The catalyst metal used was iridium because, of the active catalyst metals of group VIII, iridium best satisfies the requirements for use in field emission microscopy listed below:

1. It must be possible to fabricate sharp points from the metal. The radius of curvature of the point must be less than one micron.

2. The metal must have a high enough tensile strength to withstand a stress of some $10^9$ dynes/cm$^2$ due to the high electrostatic field.

3. It must be possible to attain clean surfaces of the metal. This implies that the metal must have a
reasonably high melting point to allow it to be heated high enough to evaporate surface oxides.

4. For studies involving the adsorption of carbon compounds there is the more stringent requirement that the melting point be high enough to allow the carbon to be removed by heating. The maximum temperature to which a field emitter can be heated is about $3/4 T_m$, the melting temperature. Dulling due to surface migration becomes excessive above that temperature. Nickel would have been a desirable metal to use since a large amount of experimental data is available on its catalytic behavior. Unfortunately its melting point is so low that a carbon contaminated nickel emitter is nearly impossible to clean (25).

Ultra-high Vacuum Techniques

The difficulties in maintaining a clean surface have been briefly described. A vacuum of better than $10^{-9}$ mm Hg was said to be necessary to preserve a clean surface for periods longer than a few seconds. Field emission microscopy also requires pressures of this magnitude since higher pressures lead to emitter failure. With the equipment used in this work, it was a routine matter to obtain and measure pressures of $10^{-10}$ mm or better. In experiments carried out at 4 °K it was possible to maintain an atomically clean surface
indefinitely.

Such techniques have only become known within the past ten years. In 1953 Alpert (26) described in some detail the methods for obtaining ultra-high vacuum. His chief contribution was the introduction of an ionization gauge which could measure pressures as low as $10^{-11}$ mm. The main difference between a Bayard-Alpert gauge and a conventional ion gauge is the reduction in size of the ion collector. In a conventional gauge the collector completely encircles the filament and grid, while in the B-A gauge the collector is a fine wire down the axis of the grid assembly. The greatly reduced solid angle subtended by the collector minimizes the number of x-rays which strike it. The number of impinging x-rays determines the residual collector current and thus the lowest pressure the gauge can measure. The B-A gauge has a residual current of about $10^{-12}$ amperes corresponding to a pressure of $10^{-11}$ mm Hg.

An additional feature of the B-A gauge is its ability to act as a pump. This pumping action appears to be the result of several simultaneous mechanisms. One of these is the formation of free atoms by the hot gauge filament with subsequent adsorption of the atoms on the walls of the gauge. Further pumping action arises from the formation of gas ions which are then accelerated toward the gauge walls by the negative potential at which the walls are normally maintained (27).
The ions arrive at the walls with sufficient velocity to penetrate below the surface. A slow deposition of evaporated tungsten from the filament provides a getter film on the walls which further enhances the pumping action. However, below about $10^{-9}$ mm Hg the pumping action is counterbalanced by a re-evolution of gas from the tube walls due to the heating action of the filament.

The vacuum system used in this work was of all-glass construction, using a two-stage mercury diffusion pump backed by a rotary forepump. Following the diffusion pump were two cold traps, separated from the working area by a magnetically operated glass valve. The entire system beyond the first trap could be enclosed in portable ovens and baked to drive off adsorbed gas. The working area contained a Bayard-Alpert gauge and the microscope tube. Gas to be used in adsorption studies was kept in a glass ampoule provided with a break-tip and separated from the working area by a bakeable all-metal valve.*

Evacuation of the system was done in the following way. The system was initially pumped down to about $10^{-6}$ mm Hg with the diffusion pump. Then the ovens were placed in position and the temperature raised to 450 °C slowly enough so that the system pressure did not increase above $10^{-5}$ mm Hg. The system, *Manufactured by the Granville-Phillips Company, Pullman, Washington.
including the second cold trap, was maintained at 450° until
the pressure fell to less than $10^{-6}$ mm Hg. Eight hours was
usually sufficient when the system had been only briefly at
atmospheric pressure. With the ovens shut off but still in
place, outgassing of the ion gauge was started cautiously.
In this way most of the gas given off by the gauge was re­
moved while the system was too hot for adsorption on the
walls. The second trap was then cooled with liquid nitrogen
and the ovens were removed. Further outgassing of the ion
gauge was continued and all other filaments were flashed
until the pressure fell to less than $10^{-8}$ mm.* The ion
gauge was then turned on and the pressure rapidly fell to
about $5 \times 10^{-10}$ mm. After a few hours the pressure was
about $10^{-10}$ mm Hg where it could be maintained for a period
of days. Most of the pumping at this pressure was due to the
diffusion pump and not to the ion gauge. This was demon­
strated by the fact that the pressure decreased further when
the ion gauge was operated only intermittently. That mercury
diffusion pumps are capable of producing much lower pressures
than had previously been realized was shown by Venema (28)
who was able to obtain a pressure of $10^{-12}$ with a specially
designed pump.

The above discussion by no means exhausts the subject

---

*If the system had been shut down for an extended period, it was often necessary to bake it again for two or three hours.
of the attainment of ultra-high vacuum. It does illustrate
the basic principle of vacuum work: the ultimate pressure in
a system is determined by a balance between pumping speed and
gas evolution. Pumping speed decreases with pressure; there­
fore, the rate of gas evolution must also be reduced to
attain very low pressures. This is accomplished by extensive
outgassing of all surfaces in the system. A more complete
discussion of these techniques is given in references (26) and
(29).

Construction of Field Emission Microscopes

Winkel (30) and Gomer (15) have discussed in some detail
the construction of field emission microscopes. The discus­
sion here will outline the techniques the author has found
most useful and describe in more detail any innovations which
were helpful.

The tungsten-glass seals were made from 40 mil sealing
grade tungsten and Corning 3320 uranium glass. The tungsten
was outgassed with a torch, cleaned with NaNO₂, then pre­
oxidized to a deep purple and sealed in a sleeve of Corning
3320. Press seals using Corning 3320 were then constructed
from this beaded tungsten. These seals were quite reliable
and withstood temperatures from 4 °K to 750 °K. Occasionally
lengths of 30 mil nickel wire were fused directly to the
ends of the tungsten leads prior to sealing. This was done
to make good electrical contact with the leads, since it is not possible to solder to tungsten. Nickel is the only metal which can easily be welded to tungsten. The inner ends of the leads were electrolytically cleaned and polished in 1 N NaOH using 10 volts d.c. Following this, a 10 mil layer of nickel was plated on the tungsten from a Watts type bath (31). This plating served to protect the tungsten from oxidation during outgassing and also made it possible to spotweld iridium wires to the leads.

The inner portion of the microscope tube was coated with a transparent conductive film to avoid the accumulation of electrostatic charge on the walls during operation. This coating was made by blowing vapors of SnCl₂ into the tube while holding it at 450 °C (15). The clearest and most conductive films were deposited using oxygen for the carrier gas. It was necessary to cover with aquadag all portions of the tube which were not to be coated. In particular, the ends of all tubing which will later be sealed must be protected, for good seals cannot be made with the coated glass. It is impossible to remove this coating after it has been applied.

Electrical connection to the coating was made with a 3/4-inch beaded tungsten lead sealed through the tube wall. Best results were obtained if a shoulder of Corning 7740 Pyrex glass was welded around the lead prior to sealing. The inner end of the lead was electrolytically etched off flush
with the surface, then plated with a thin layer of nickel. Silver paste (Dupont #4760) was painted over the inner end of the lead and the surrounding area. After drying, the paste was fired at 600 °C; the tube was then cooled to 450° and the conductive coating applied.

The fluorescent screen was applied by the lacquer flow method. Five gm Sylvania #2282 phosphor (willemite) was suspended in 5 cc of amyl acetate and 5 cc of clear lacquer. The mixture was milled for several hours with glass beads agitated by a magnetic stirring bar. Three drops of heptanoic acid were added to stabilize the slurry. The phosphor slurry was then spread evenly over the surface to be coated, the excess was poured off and the screen allowed to dry. After air-drying overnight, the screen was slowly heated to a final temperature of 500 °C. This treatment burned off all the organic binder leaving only the phosphor.

The filament assembly is shown in Figure 2. The filament is 5 mil iridium; the temperature-sensing leads and emitter are 2 mil iridium. The assembly was made by first spotwelding the emitter blank to the hairpin filament (30); then the sensing leads were attached. The assembly was then spot-welded to the four tungsten leads. The final step was the etching of the emitter.

The etching of field emitters is one of the more difficult techniques to learn. Each metal used in the microscope
Figure 2. Field emission microscope for operation in a liquid helium cryostat
requires different methods for etching which can generally be found only by trial and error. Iridium is a particularly difficult metal to etch because of its great resistance to chemical attack. Winkel developed a flame-etching technique (30) which produces very sharp points ($r < 5000 \, \AA$). Unfortunately these points are often rather badly contaminated. An electrolytic etch bath which was used with some success was made by fusing a mixture of two parts (by weight) KNO₃ and three parts KOH in a platinum crucible. The optimum bath temperature (which was rather critical) was about 430 °C. About 0.3 volts a.c. was applied between the crucible and the emitter blank. By slowly withdrawing the emitter from the bath the proper taper could be obtained. However, these points were not always as sharp as could be desired.

The most successful method for producing clean, sharp emitters involved both a flame etch and a chemical etch. The wires to be used in the filament assembly were cleaned by etching in a bath of fused KCl-NaCl contained in a ceramic crucible. About 5 volts a.c. was applied between the wire to be cleaned and an iridium electrode dipping in the bath. The wires were then welded together and the filament assembly welded to the tungsten leads. The assembly was washed in aqua regia to remove any copper contamination introduced by the spot-welder, then briefly etched again in the chloride bath and carefully washed with re-distilled water. A microtorch
with an oxy-hydrogen flame was used to flame polish the assembly, and the protruding ends of the emitter and temperature-sensing leads were melted back to form spherical caps. This insured that no spurious emission could occur from possible sharp edges. The emitter was then flame-etched following Winkel's procedure. A small portion of the end of the emitter was then etched away with a very brief voltage pulse (0.3 v. for 0.5 sec) in the fused KOH-KNO₃ bath. The entire assembly was carefully washed in redistilled water for a few minutes to remove all traces of salt. This treatment usually produced very clean emitters which were adequately sharp.

Temperature Control

For kinetic studies of surface reactions and desorption it is naturally essential to know the surface temperature quite accurately. The temperature of the emitter in a FEM can be measured by using a portion of the filament as a resistance thermometer (32). It is also desirable to be able to raise the temperature of the emitter to any predetermined value as rapidly as possible in order to observe the temperature dependence of reaction rates.

With the circuit shown in Figure 3 it is possible to raise the filament temperature by electrical heating to any desired value in about one second. The temperature can be
Figure 3. Filament heating circuit

- $T_1$: 110V FILAMENT TRANSFORMER
- $T_2$: 5V FILAMENT TRANSFORMER
- $R_1$: 0.3Ω WOUND FROM 15 MANGANIN
- $R_2, R_3$: 1000Ω PRECISION WIREDOWN
- $R_4, R_5$: 1000Ω HELIPOT
- $C_1$: 0.001µF CAPACITANCE
- $SW_1, SW_2$: DPDT TOGGLE SWITCH
- $SW_3$: DPST TOGGLE SWITCH
- Amplifier Heath Model A-9C
- Microscope
measured to ± 2 °K over the range of calibration. The de-
tecting circuit is a Kelvin double bridge which measures the
resistance r across the central portion of the filament. If
the resistances \( R_4 \) and \( R_5 \) are varied in such a way that

\[
\frac{R_4}{R_2} = \frac{R_5}{R_3}
\]

then the bridge has a unique balance when (33)

\[
\frac{r}{R_1} = \frac{R_4}{R_2} = \frac{R_5}{R_3}
\]

which is independent of the resistance of the rest of the
filament. The energizing current to the bridge, furnished by
the powerstat, heats the filament to some final temperature
which depends on the powerstat setting. This current is
applied when SW-1 is closed. To speed up the heating rate,
SW-2 can be closed, applying feedback to the circuit. In this
mode, the bridge error signal is amplified and added in phase
to the powerstat current. As the filament is heated, its
resistance increases, the bridge approaches balance and the
feedback signal is reduced. The feedback mode also compen-
sates for line voltage fluctuations. When the filament be-
comes too hot, an out-of-phase signal is generated which re-
duces the current. The amount of feedback is varied by the
amplifier volume control and is adjusted for the maximum
value which does not cause overshooting when the current is
applied. Balance and overshooting are indicated by the null
detector. \( R_4 \) and \( R_5 \) determine the balance condition and are always set to the same value so that Equation 41 is satisfied.

Thus the bridge can be used either for measuring the resistance \( r \), or for heating the filament to some final value of \( r \). If the dependence of \( r \) on filament temperature is known, the bridge can be used to measure and control the filament temperature. Klein and Simpson (34) have described a somewhat more complicated circuit using direct current for heating the filament.

A measurement of \( r \) which does not depend on the resistance of the rest of the filament is necessary since large temperature gradients may exist along the filament. For example, the tungsten leads may be at 4 °K while the central portion of the filament is at 1000 °K. To analyze this situation more carefully, it is necessary to know the temperature distribution along an electrically heated wire whose ends are maintained at some fixed temperature. This problem has been solved by Rowland (35) using the assumptions that resistance and thermal conductivity are constant, and that heat loss is due to conduction along the wire and radiation alone. At temperatures where radiation losses are negligible he showed that

\[
\frac{T - T_0}{T_{cm} - T_0} = 8 \left\{ \frac{x/L - x^2/L^2}{2} - \frac{4}{\pi^3} \sum_{m=1,3,5,\cdots} \frac{\sin m\pi x/L}{m^3} \exp \left[ \frac{-m^2 \pi^2 kt}{L^2} \right] \right\}
\]

(43)
where \( T_0 \) is the temperature at the ends of the wire, \( T \) the temperature at a point \( x \) cm from the end, \( T_{cm} \) the temperature at the center when \( t \) becomes very large, \( t \) is the time after a steady current is applied, \( L \) the length of the wire and \( \kappa \) the thermal diffusivity, i.e.,

\[
\kappa = \frac{K}{dC} \text{ cm}^2 \text{ sec}^{-1}
\]

(44)

where \( K \) is the thermal conductivity, \( d \) the density and \( C \) the specific heat. As \( t \) becomes large

\[
\frac{T-T_0}{T_{cm}-T_0} = 4 \left( \frac{x}{L} - \frac{x^2}{L^2} \right)
\]

(45)

Let us assume that the temperature distribution along a heated filament of a FEM is given by Equation 45; furthermore, assume that the resistivity of the wire is a linear function of \( T \), i.e.,

\[
\rho(T) = \alpha T + \beta
\]

(46)

Then from Equation 45

\[
\rho - \rho_0 = 4\alpha (T_{cm} - T_0) \left( \frac{x}{L} - \frac{x^2}{L^2} \right)
\]

(47)

The filament dimensions were such that \( x/L = 0.45 \) at a sensing lead and 0.5 at the emitter. If \( x_1 \) and \( x_2 \) denote the positions of the sensing leads then the resistance \( r \) of the end of the filament is

\[
r = \int_{x_1}^{x_2} \frac{1}{a} \rho dx = \frac{2L}{a} \int_{x_1}^{x_2} \left[ 4\alpha (T_{cm} - T_0) \left( \frac{x}{L} - \frac{x^2}{L^2} \right) + \rho_0 \right] d\left( \frac{x}{L} \right)
\]

(48)

where \( a \) is the cross-sectional area of the filament.
Then
\[ r = 0.09966 \frac{L}{a} \alpha (T_{cm} - T_0) + 0.1 \frac{L}{a} \rho_0 \] (49)

Using Equation 46
\[ r = 0.09966 \frac{L}{a} (\alpha T_{cm} + \beta) + 0.0034 \frac{L}{a} (\alpha T_0 + \beta) \] (50)
\[ = 0.1 \frac{L}{a} (\alpha' T_{cm} + \beta') \] (51)
and thus \( r \) is a linear function of \( T_{cm} \). Now if the entire filament is at \( T_{cm} \)
\[ r = r_{cm} \int_{x_1}^{x_2} \frac{L}{a} \rho_{cm} dx = \frac{2L}{a} \int_{x_1}^{x_2} (\alpha T_{cm} + \beta) dx \] (52)
\[ = 0.1 \frac{L}{a} (\alpha T_{cm} + \beta) \] (53)

From Equations 50, 51
\[ \alpha' = 0.9966 \alpha \]
\[ \beta' = \beta + 0.0034 \alpha T_0 \] (54)

Now in practice the filament was calibrated by immersion in a constant temperature bath so that the entire filament was at some \( T_{cm} \). From measurements of \( r_{cm} \) at various temperatures \( \alpha \) and \( \beta \) were determined. When the microscope was in operation however, the quantity measured was \( r \) and not \( r_{cm} \). We can now determine the error in \( T \) calculated from \( r \) using \( \alpha \) and \( \beta \). Let us choose the worst possible conditions by letting \( T_0 = 0 \ ^\circ K \), \( T_{cm} = 600 \ ^\circ K = T_{calc} \). Then \( \beta' = \beta \) and from Equations 51 and 53
\[ T_{true} = \frac{\alpha}{\alpha'} T_{calc} = 1.003 \times 600 = 602 \ ^\circ K \] (55)
This is considered the maximum error because above 600 \( ^\circ K \)
radiation heat loss becomes important. This tends to even out the temperature distribution along the filament since the heat loss is proportional to $T^4$. One may question whether the assumption of constant resistance used in the derivation of Equation 43 will affect its validity. Ehrlich (23) has measured the resistance along sections of a tungsten flash filament whose ends were held at 77 °K. The measurements were made both during a flash and after a steady state had been reached. Values of the section resistances calculated from Equation 45 agreed well with his observed steady state values. Ehrlich's results also indicated that during a flash desorption experiment the temperature along a filament is very nearly constant except for a small section near the ends. Calculations from Equation 43 using $t = 1$ second agree with his results. For a filament 10 cm long whose ends are held at 77 °K, only in the 5 mm sections at each end are there any appreciable temperature gradients when the central temperature is less than 500 °K. This uniform temperature is obtained because, during a flash, the rate of heat generation in the wire is very much greater than the rate of heat loss through the ends. It can be seen from Equation 43 that this will be the case when $\frac{m^2 \pi^2 x t}{L^2}$ is small. Thus in flash filament desorption no great error results from the assumption that the filament is entirely at a uniform temperature.
We have assumed that the resistivity of the filament is linear with $T$. This was established by immersing an annealed filament in a constant temperature bath and measuring the resistance. The temperature of the bath was measured with a calibrated thermocouple and a Leeds and Northrup #8662 potentiometer. Over the range from 77 °K to 608 °K the plot of $R$ vs. $T$ was linear to within two degrees. This filament was found to have a temperature coefficient of $1.23 \times 10^{-4}$ ohms/degree and a resistance of 0.0295 ohms at 273 °K for the 7 mm center section. Since the dimensions of the wire were not known with any great precision, the resistivity was not calculated. The temperature coefficient of resistivity $\alpha$ is independent of filament dimensions, and for this filament $\alpha$ was $4.17 \times 10^{-3}$ degrees$^{-1}$. $\alpha$ was found to vary slightly for the different filaments so that individual calibrations were necessary.

A final source of error in the bridge circuit must be considered. $r$ is determined from the value of $R_4$ (or $R_5$) at balance according to Equation 42. From Figure 3 it can be seen that $R_4$ should really include the resistance $r_4$ of the temperature sensing lead, i.e.,

$$R_4 = R'_4 + r_4$$

(56)

where $R'_4$ is the apparent value read from the dial. This also is true for $R_5$,

$$R_5 = R'_5 + r_5.$$

(57)
But $r_5 = r_4$ from the symmetry of the filament assembly, and since $R_5 = R_4$ always, the conditions of Equation 41 are maintained. Thus

$$r = R_1 \frac{R_4}{R_2} = R_1 \frac{R'_4}{R_2} + R_1 \frac{r_4}{R_2}$$

(58)

The magnitude of this correction to $r$ can be estimated from measured values of $r_4$ at various temperatures. At 600 °K $r_4$ is about 1.5 ohms which causes a change in $r$ corresponding to about 3°. If the conditions during operation were the same as those during calibration this would not matter. In the experiments, however, the ends of all the leads were maintained at a constant temperature so that a temperature gradient existed along the sensing lead. If we again pick the most drastic conditions, we can assume that the entire sensing lead is at 4 °K, in which case $r_4 = 0$. Then for a given dial setting $R_4$, $r$ will be lower by an amount $(R_1/R_2)r_4$ from the calibrated value, and at 600 °K this was said to correspond to 3°.

To sum up, temperature gradients along the filament cause the actual temperature at the emitter to be higher than the apparent temperature determined from calibration. Gradients along the sensing leads cause the actual temperature to be lower than the apparent temperature. The errors introduced are small and from estimates at 600 °K appear to cancel. Thus it seems safe to say that the emitter temperature could be measured to ± 2°, which is the estimated precision of the
potentiometers $R_4$ and $R_5$, from 77° to 600 °K. Above 1000 °K the temperature at the end of the emitter is less than the temperature of the filament because of radiation loss along the emitter. For accurate work at high temperatures a correction for this loss must be made.

Low-temperature Experiments

Another method by which ultra-high vacuum can be obtained is cryogenic pumping. If a sealed-off FEM is placed in a liquid helium cryostat all gases in the tube other than helium will condense on the walls. Gomer has estimated (15) that the pressure inside such a tube is less than $10^{-15}$ mm Hg if helium is excluded. To study adsorption, one can fill a tube with a small amount of the desired gas, seal the tube and place it in a liquid helium cryostat. If the helium is added in such a way that one portion of the tube is cooled first, all of the gas in the tube will condense at that spot and the pressure inside the tube will become negligible. If the part of the tube which is covered with condensed gas is warmed briefly, some of the gas can be distilled onto the field emitter. All the gas molecules missing the emitter strike the cold walls of the tube and stick. Thus the pressure in the tube remains so low that no molecules strike the emitter except when the gas deposit is intentionally warmed.

The microscope tube in Figure 2 was constructed for use
in a helium cryostat. For clarity, the filament assembly and tungsten support leads have been rotated 90° with respect to the emitter and the rest of the tube. In the actual tube the emitter was directed normal to the plane of the filament assembly. The cold finger at the top of the figure was the gas source. The manganin coil was heated electrically to evaporate doses of gas deposited on the bottom of the finger. The silver anode was a thin ring of DuPont #4760 paste outlining the fluorescent screen and making electrical contact to the tungsten anode lead. Its purpose was to insure a uniform field.

Figure 4 shows the helium cryostat. A is the microscope tube in position, B is a brass funnel used to direct the liquid helium arriving through the transfer port D into the cold finger C. E are the six electrical leads to the filament assembly and heating coil. F is the high voltage lead which is enclosed in an evacuated glass tube for electrical insulation. This arrangement avoids corona discharge and provides a fairly small heat leak. G is a styrofoam float which indicates the liquid level. H is the unsilvered window for viewing the emission patterns. I leads to a vacuum pump and relief valve. J is used to evacuate the jacket of the helium dewar. K is the brass header used to support the helium dewar. The dewar has a flat lip which is seated between two neoprene gaskets and clamped in place, thus holding the dewar
Figure 4. Liquid helium cryostat for field emission microscopy
in position and maintaining a vacuum seal. L is the filling port and M is an aluminum header for the nitrogen dewar. M is seated on a neoprene sponge gasket and sealed around the helium dewar with an O-ring. When photographs are taken of emission patterns, L is closed. Pressure builds up in the nitrogen dewar which stops the boiling, allowing an unobscured view of the microscope face.

A tube intended for use in the cryostat was first evacuated to $10^{-10}$ mm Hg as previously described. High voltage was applied and the emission pattern was inspected for cleanliness. Then, with the voltage off, the gas ampoule was broken and the hydrocarbon was distilled onto the cold finger which was filled with liquid nitrogen. The tube was then sealed off and placed immediately in the cryostat. Liquid nitrogen was added to the outer dewar and the jacket of the helium dewar was filled with nitrogen gas for heat transfer. When the tube was cooled to 77 °K (indicated by the filament resistance), the jacket was evacuated and liquid helium was added. It was necessary to insure that gaseous helium came in contact only with cold tubes (77°), since helium diffuses through Pyrex rather quickly at room temperature (29, 36). The two liters of helium contained in the cryostat lasted from four to six hours. If the microscope tube were to be used again, it was stored under liquid nitrogen.

The book by White (37) is recommended for a detailed
discussion of cryogenic techniques.

Flash Filament Experiments

Figure 5 shows a tube used for flash filament studies. Attached to the filament was a field emitter so that the emission pattern could be observed during the adsorption process. In the figure the filament assembly has again been rotated with respect to the emitter and screen. Gas was admitted from one side of the tube and pumped out the other through magnetically operated glass valves which could be closed to seal off the tube from source and pumps during a flash. The tube was constructed with a reservoir just above the filament assembly which could be filled with water or liquid nitrogen to maintain the filament at a fixed temperature during adsorption.

The tubes were pumped down in the usual manner. Particular care was given to the outgassing of the ion gauge attached to the tube. When the system pressure was $1 \times 10^{-10}$ mm Hg or less, the Granville-Phillips valve was closed and the gas ampoule was opened. The valve was then carefully opened until the pressure in the tube increased to about $5 \times 10^{-9}$ mm. The filament was flashed, then allowed to adsorb gas for varying periods. Then the glass valves were closed and the filament was flashed from a constant voltage source. The pressure rise indicated by the B-A gauge was recorded on a Moseley Model 3-S x-y recorder using a linear time sweep of 2 in/sec.
Figure 5. Field emission microscope for flow system and flash desorption experiments
Temperature calibration was accomplished by using the reservoir as a constant temperature bath while measuring filament resistance with the bridge circuit. The temperature increase during a flash was established by recording the time dependence of the bridge unbalance signal for various values of $R_4$ and $R_5$.

The ion gauge was calibrated against a McLeod gauge for hydrogen. The sensitivity $S$, defined by

$$i_C = i_g S P,$$

where $i_C$ is the ion current, $i_g$ is the emission current and $P$ the pressure in mm Hg, was $5 \text{ mm}^{-1}$. The calibration was probably not very precise since the ranges of the McLeod gauge and ion gauge overlap only at the extreme lower and upper pressure limits respectively. However, this value is in good agreement with the gauge constant of $4.4 \text{ mm}^{-1}$ used by Hickmott for a similar gauge. From Equations 37 and 39 it can be seen that an error in the gauge sensitivity affects only the value for $n_0$, the number of molecules adsorbed per cm$^2$. $n_0$ is already uncertain since the true area of the filament is not known exactly. The true (or effective) filament area is the geometric area multiplied by a roughness factor minus the area of the end portions which remain cool during a flash. Thus $n_0$ is probably uncertain by $\pm 20\%$. 

RESULTS

Field Emission from Clean Iridium

The criteria for the cleanness of a field emitter are the following:

1. Emission patterns from clean emitters do not show a great amount of surface structure. The pattern consists of fairly uniform dark and bright patches, which correspond to low index facets and rounded, higher index regions respectively.

2. Clean emission patterns show temperature stability, i.e., if the filament is flashed or annealed at elevated temperatures, the emission pattern does not change appreciably.

3. The emission characteristics are reproducible. Clean emitters of a metal all have similar emission patterns and work functions.

These criteria have been established primarily from experimental work with tungsten field emitters, but clean surfaces of other refractory metals have been examined in the field emission microscope, i.e., molybdenum, niobium, tantalum, rhenium and nickel. When very small amounts of material are allowed to adsorb on these clean surfaces, striking changes in emission patterns occur. Generally, the patterns show much more structure than do the clean patterns, since adsorption does not occur uniformly over the surface. Bulk impurities
can be observed as diffusion to the surface occurs. Since the emission patterns show such marked effects with adsorption, one feels justified in assuming that patterns which do not show these effects are from clean surfaces. Work by Müller (38) with the field ion-microscope which can resolve individual surface atoms has verified that atomically clean surfaces of these metals can be obtained.

Clean iridium field emitters were prepared using the techniques described in the last section. It was surprisingly difficult to obtain clean iridium. The iridium wire used was obtained from Engelhard Industries, and a spectrographic analysis supplied by the manufacturer revealed that the principal impurities were:

\[
\begin{align*}
\text{Pd} & \approx 0.046\% \\
\text{Fe} & \approx 0.01\% \\
\text{Pt} & \approx 0.02\% \\
\text{Rh} & \approx 0.016\% 
\end{align*}
\]

These impurities were all metals fairly similar to iridium and were not expected to modify the emission characteristics to any great extent. In view of the flame-etching technique which was used the principal surface impurity was expected to be oxygen. The oxides of iridium decompose at about 1200 °C so that heating above that temperature should have been sufficient to clean the surface. Nevertheless it was often impossible to clean a flame-etched emitter completely even by heating to 2200 °C. The additional chemical etch was usually sufficient to produce emitters which could be cleaned by
flashing; moreover, these clean emitters remained clean after extensive heat treatments. This was taken as evidence that bulk impurities in the metal were not responsible for the surface contamination, since diffusion of impurities to the surface should become noticeable at high temperatures. The flame etch and electrolytic etch both produce iridium oxides; since either etch used alone usually produced contaminated surfaces, the contamination was probably oxygen. It is very surprising, however, that this could not be removed at 2200-2400 °K.

Another unusual feature of iridium was that flame-etching invariably produced emitters with a nearly 100 crystallographic orientation, i.e., the emitter axis was nearly parallel to the ⟨100⟩ direction. On the other hand, chemical etching of the unannealed wire usually produced emitters with a 111 orientation. Emitter blanks which had been annealed by flame-polishing produced 100 oriented emitters upon chemical etching. Thus the annealing process appeared to change the crystallographic orientation of the wire. When iridium wire was heated above 1200 °C extensive grain growth was observed. The crystal grains extended across the entire wire diameter, and the wire fractured very easily at the grain boundaries. It seems plausible that the growth of 100 oriented grains may have been favored over other orientations.

Figures 6a and 6b show the emission from clean 100 and
Figure 6a. Clean, 100 oriented iridium field emitter

Figure 6b. Clean, 111 oriented iridium

Figure 6c. Crystallographic map for 100 oriented fcc field emitter
110 oriented emitters respectively. Figure 6c is a crystallographic map for a 100 oriented face-centered cubic emitter. By comparing the emission pattern with the map, one observes that the close-packed 100 and 111 planes are well-developed with high work-functions. The 110 planes are only slightly developed. These patterns are nearly identical to those reported by Wortman et al. (39) for clean nickel.

The current-voltage characteristics were measured for a clean iridium emitter at 4 °K. The emission current I was measured with an Applied Physics Model 31-CV electrometer while the applied voltage V was measured potentiometrically across a 100Ω section of a 20 MΩ voltage divider connected in parallel with the microscope.

From these data the average work function for a clean iridium emitter was obtained using the method of Bradley and D'Asaro (40). From Equation 13 the Fowler-Nordheim equation can be written

\[ J = (1.54 \times 10^{-6} F^2/\varphi) \exp \left[ -6.83 \times 10^7 \varphi^{3/2} t(y)/F \right] \] (59)

upon setting \( t(y) = 1 \). Using Equation 59, a plot was made of log \( J \) vs. log \( F \) for various values of \( \varphi \). From Equations 15 and 16

\[ \log I = \log J + \log A \] (60)

\[ \log V = \log F - \log \beta \]

The experimental data were plotted in the form log \( I \) vs. log \( V \). An arbitrary value of \( \varphi \) was chosen and the experimental curve
was fitted to the theoretical curve corresponding to this \( \Phi \). From the intersection of the axes of the two curves, approximate values were obtained for \( A \) and \( \beta \) using Equation 60. Next, the experimental data were plotted in the form \( \log I/V^2 \) vs. \( I/V \). From Equations 59 and 60 it follows that the slope

\[
S = \frac{d \log I/V^2}{d \log 1/V} = -2.97 \times 10^7 \Phi^{3/2} \frac{s(y)}{\beta}
\]

where \( s(y) = f(y) - \beta \frac{df(y)}{dy} \) and \( y \) is given by Equation 14. Tables of \( s(y) \) and \( f(y) \) have been published (9). From Equation 61 a corrected \( \Phi \) was calculated, using the approximate value for \( \beta \) and the measured slope \( S \). Then the entire process was repeated using the theoretical curve corresponding to the corrected \( \Phi \). After repeating the process two or three times a self-consistent value for \( \Phi \) was obtained, i.e., the calculated \( \Phi \) agreed with the assumed \( \Phi \). The final values of \( \Phi \), \( \beta \), and \( A \) were:

\[
\Phi = 4.65 \text{ ev} \\
\beta = 9.95 \times 10^5 \text{ cm}^{-1} \\
A = 3.1 \times 10^{-9} \text{ cm}^2
\]

The treatment described above is really valid for a surface with a single work function only. For a patchy surface we defined an average work function by Equation 20. Equation 20 can be written

\[
\frac{I}{V^2} = (1.54 \times 10^{-6} \beta^2 \frac{A}{\Phi}) \exp \left[ -6.83 \times 10^7 \Phi^{3/2} \frac{f(\bar{y})}{\beta V} \right]
\]
by analogy with Equation 59. ($\bar{y}$ is obtained by replacing $\phi$ with $\bar{\phi}$ in Equation 14.) Similarly
\[
S = \frac{d \log I/V^2}{d (1/V)} = -2.97 \times 10^7 \, \bar{\phi}^{3/2} \, s(\bar{y})/\beta \quad (63)
\]
Now Equations 62 and 63 are of the same form as Equations 59 and 61 so that the treatment of experimental data given above is still valid. However, the quantities determined are $\bar{A}$ and $\bar{\phi}$, where $\bar{\phi}$ is defined by Equation 63 and $\bar{A}$ by Equation 62.

Using Equation 19 it can be shown that
\[
\bar{A} = \sum_i A_i \bar{\phi}/\phi_i \exp \left[ (\Delta \bar{\phi}^{3/2} - b_i \phi_i^{3/2})/V \right] \quad (64)
\]
It has previously been shown that $\bar{\phi}$ is very nearly equal to the smallest $\phi_i$ on the surface. From Equation 64 it can then be seen that $\bar{A}$ is very nearly the area of the patch with the lowest $\phi_i$. This is most nearly true for a surface containing fairly uniform low work function patches along with patches of much higher $\phi_i$. Figure 6 shows that this is the case with clean iridium. In fact, any significant contribution of higher work function patches to $\bar{\phi}$ would result in non-linear behavior in the Fowler-Nordheim plot of $\log I/V^2$ vs. $1/V$. The emission data are shown in Figure 7 plotted both as $\log I$ vs. $\log V$ (curve I) and $\log I/V^2$ vs. $1/V$ (curve II). The solid line in curve I was calculated from Equation 59.

A second way to determine the work function of a field emission cathode involves a determination of the field factor $\beta$ from a microscopic examination of the shape and size of the
Figure 7. Emission characteristics of clean iridium
end of the emitter. If $\beta$ is known, $\Phi$ can be calculated from Equation 63. To determine $\beta$, the field at the end of the cathode must be determined from the emitter geometry using potential theory. Drechsler and Henkel (41) approached the problem by superimposing the potential at a spherical surface onto the potential at the surface of a hyperboloid of revolution, the object being to obtain equipotential surfaces which fit observed emitter shapes. Heat treatment generally causes the end of actual emitters to become somewhat bulbous. By varying the fraction of spherical potential included, they were able to obtain equipotential surfaces which were very similar to actual emitter surfaces. By taking the gradient of the potential at the apex they obtained the field. In terms of the parameter $\gamma$ representing the fraction of spherical potential, the field at the apex was shown to be

$$F = V\left[ \frac{\gamma}{r} + \frac{2(1-\gamma)}{r \ln \left( \frac{4R}{r} \right)} \right]$$

(65)

where $r$ is the radius of the emitter and $R$ the cathode-to-screen distance.

The emitter previously described was removed from the microscope and examined at 1800X magnification in a metalurgical microscope. The tip radius was estimated to be 3000Å; from the curves given by Drechsler and Henkel the spherical factor $\gamma$ was estimated at 0.15. Since $R$ was 2.8 cm,
from Equation 65 $\beta$ was $9.43 \times 10^3$. Then using the slope of the Fowler-Nordheim plot, $\phi$ was found to be 4.5 ev.

Neither of these methods is a very precise way for calculating the work function. The method of Bradley and D'Asaro depends on the accuracy with which the experimental data can be fitted to a theoretical curve. In this work the accuracy was estimated at $\pm 1\%$ or 0.05 ev, though Bradley and D'Asaro estimated an accuracy of $\pm 0.5\%$ for $\phi$. The method of calculating the field at the emitter is much less accurate due to errors in estimating $r$ and $\gamma$. The accuracy of $\phi$ by this method was probably $\pm 15\%$. It is, however, interesting to note that if the end of the emitter were a hemisphere with a radius of 3000 Å, the surface area would be $5.7 \times 10^{-9}$ cm$^2$. The effective emitting area obtained from the curve-fitting method was $3.1 \times 10^{-9}$ cm$^2$ or about one-half the estimated area. Figure 6a shows that this is about the correct ratio.

The values of $\phi$ for iridium reported by other investigators are 5.40 ev and 5.30 ev by thermionic emission (42, 43) and 4.57 ev by contact potential (44). The rather large discrepancy between the field emission value and the thermionic emission values is not too surprising when one considers the types of surfaces observed. The thermionic emission measurements were made on polycrystalline wires or ribbons whose surface condition was not well known. It may be that such samples have primarily close-packed surfaces with corres-
pondingly high work function. It also seems unlikely that the methods used were sufficient to obtain clean iridium surfaces.

Field Emission from Covered Iridium

Adsorption of ethylene

Two methods were used for studying the adsorption of ethylene in the FEM. In the first method ethylene gas at a very low pressure (~$10^{-9}$ mm Hg) was allowed to stream through a field emission microscope. The emitter was cleaned by flashing, then cooled to either 300 °K or 77 °K by means of a cooling bath incorporated in the microscope (see Figure 5). When the emitter was cool high voltage was applied and the emission pattern was observed as adsorption progressed. Marked changes in emission intensity were observed; however, it soon became apparent that only qualitative information could be obtained from this experiment. Even at $10^{-9}$ mm the rate of adsorption was so rapid that with the equipment available it was not possible to measure quantitatively the changes in the work function. It was not possible to shut off the flow of ethylene by closing the valve to the gas ampoule because enough gas desorbed from the various surfaces in the system to maintain the pressure at about $10^{-9}$ mm. It was also impossible to evaluate the effects which the ionization gauge might have caused. Certainly one would expect some decomposition of hydrocarbons to occur at the hot filament of
the gauge, with subsequent adsorption of the products on the emitter. Yet it was desirable to leave the gauge operating to obtain some indication of the system pressure.

These difficulties have been described primarily to point out the advantages of the method which was finally used. Gomer (14) first described the method of operating a field emission microscope in liquid helium. There is no difficulty with changes in emission occurring during a measurement since the pressure inside the tube at 4 °K is essentially zero. This method is particularly useful with gases such as hydrocarbons which are easily decomposed. Since the hydrocarbon is kept frozen at all times while in the microscope, only a small portion ever comes in contact with the metal filament and the amount of decomposition is kept to a minimum.

The first experiments in the liquid helium cryostat were conducted in the following way. The emitter was cleaned by flashing, cooled to 4 °K, and the emission characteristics were measured. Then the tip was dosed by warming the source briefly. The filament of the microscope was then heated rapidly to a pre-set temperature, initially about 70 °K, for twenty seconds. Before the field was ever applied, the tip was allowed time to cool to 4 °K to avoid any field-enhanced surface reactions. The emission pattern was photographed and work function data were recorded (usually by measuring the voltage required to obtain a given emission current; more will
be said about this technique later). Then the filament was flashed to a slightly higher temperature for twenty seconds and allowed to cool. Again the emission characteristics were recorded. In this fashion the emission patterns and work function data were obtained as the emitter was heated in steps of about 50° from 60 °K to 1600 °K. Figures 8, 9, and 10 show the emission patterns for one such experiment.

If the dosing was done with the field applied, the emission initially increased, then decreased, as the deposit became thicker. Only rarely was it possible to obtain the sharp boundaries separating covered and uncovered portions of the emitter which Gomer observed on tungsten (14). This is probably due to the much smoother surface (on an atomic scale) of the face-centered cubic structure as compared to the looser body-centered structure of tungsten. The thermal energy which the evaporated ethylene molecules possessed was apparently enough to allow them to migrate over the emitter surface.

When the emitter was warmed slightly to 50-70 °K the work function decreased sharply, yet the pattern was quite similar to that for clean iridium except for the more pronounced 102 planes. As the flash temperature was increased little change in the pattern was apparent, but at about 300 °K the work function began to increase rapidly, reaching a maximum at about 650 °K. There were a number of very remarkable features about this behavior. The progression from negative to
Figure 8a. Clean iridium

Figure 8b. The emitter of 8a covered with ethylene and heated to 75 °K for 20 seconds

\[ \Delta \phi = -0.43 \text{ ev} \]

Figure 8c. After heating to 127 °K

\[ \Delta \phi = -0.47 \text{ ev} \]

Figure 8d. After heating to 212 °K

\[ \Delta \phi = -0.46 \text{ ev} \]

Figure 8e. After heating to 297 °K

\[ \Delta \phi = -0.46 \text{ ev} \]

Figure 8f. After heating to 383 °K

\[ \Delta \phi = -0.32 \text{ ev} \]
Figure 9a. After heating the emitter of Figure 8 to 468 °K
\[ \Delta \phi = -0.25 \text{ ev} \]

Figure 9b. After heating to 553 °K
\[ \Delta \phi = -0.07 \text{ ev} \]

Figure 9c. After heating to 638 °K
\[ \Delta \phi = +0.08 \text{ ev} \]

Figure 9d. After heating to 722 °K
\[ \Delta \phi = +0.12 \text{ ev} \]

Figure 9e. After heating to 892 °K
\[ \Delta \phi = -0.03 \text{ ev} \]

Figure 9f. After heating to 1150 °K
\[ \Delta \phi = -0.12 \text{ ev} \]
Figure 10a. After heating the emitter of Figure 9 to 1321 °K 1410 °K
\[ \Delta \varphi = -0.15 \text{ ev} \]

Figure 10b. After heating to 1400 °K
\[ \Delta \varphi = -0.17 \text{ ev} \]

Figure 10c. After heating to 1491 °K
\[ \Delta \varphi = -0.18 \text{ ev} \]

Figure 10d. After heating to 1662 °K
\[ \Delta \varphi = -0.23 \text{ ev} \]

Figure 10e. An emitter with a thick deposit after heating to 1500 °K

Figure 10f. The emitter of 10e after heating to 900 °K with field applied
positive work function change was quite unusual and has not been reported in previous adsorption studies. The fact that the emission pattern changed so slightly and was so similar to the clean pattern while the work function was changing so radically is surprising. This would seem to indicate considerable homogeneity of the emitting portion of the surface.

Above 650 °K the surface developed a grainy appearance while the work function slowly decreased. Above 1200 °K the graininess became more pronounced, with individual crystallites becoming resolved. Around 1600 °C the crystallites began to build up around the edges of the close-packed 111 planes. Finally above 1800 °K desorption began. flashes to about 2200 °K were necessary to clean the surface completely.

Figure 11 shows how the work function changed with the flash temperature. The work functions were obtained using the approximate equation given by Klein (45)

$$\Phi_1 = \Phi_0 \left[ \frac{V_1}{V_0} \right]^{2/3}$$

where $\Phi_0$ is the work function of the clean metal, $V_1$ and $V_0$ are the voltages necessary to obtain a given current (in this case $10^{-6}$ amperes) from the covered and clean surfaces respectively.

To test the validity of this equation it is necessary to refer to the Fowler-Nordheim equation again. For an emitter giving the same current at different values of $\bar{\Phi}$ and $V$, it
Figure 11. Change in work function with flash temperature for ethylene on iridium.
follows from Equation 62
\[ \frac{A_1}{\bar{\Phi}_1} V_1^2 \exp[-6.83 \times 10^7 \frac{\bar{\Phi}_1}{\Phi_1} \frac{f(\bar{y}_1)}{\beta V_1}] \]
\[ = \frac{A_o}{\Phi_0} V_o^2 \exp[-6.83 \times 10^7 \frac{\Phi_0}{\bar{\Phi}_0} \frac{f(\bar{y}_0)}{\beta V_o}] \]  
(67)

It is easily shown that
\[ \bar{y}_1 \approx \bar{y}_2 \]
and thus
\[ f(\bar{y}_1) \approx f(\bar{y}_2) \]  
(68)
using Equations 14 and 66. Now if we assume that the emitting area remains constant, \( \bar{A}_1 = \bar{A}_o \), and from Equation 67
\[ \frac{\beta V_1}{6.83 \times 10^7} = \frac{\bar{\Phi}_1^{3/2}}{\bar{\Phi}_0^{3/2}} \frac{V_1}{V_o} \]
(69)

The left-hand term is small, and denoting it by \( \delta \) we can write
\[ \bar{\Phi}_1 = (\bar{\Phi}_0^{3/2} \frac{V_1}{V_o} + \delta)^{2/3} \]
(70)
Since \( \delta \) is small we can expand Equation 70 in a Taylor's series. Let
\[ \Phi_1^* = \bar{\Phi}_0 (\frac{V_1}{V_o})^{2/3} \]
(71)
then
\[ \bar{\Phi}_1 = \Phi_1^* + \frac{2}{3} \delta (\Phi_1^*)^{-1/2} + \ldots \]
(72)
\( \delta \) can be evaluated using the approximation that \( \bar{\Phi}_1 \approx \Phi_1^* \)
\[ \delta = \frac{V_1 \beta}{6.83 \times 10^7} (\ln \frac{\Phi_o}{\bar{\Phi}_1} + 2 \ln \frac{V_1}{V_o}) = \frac{F_1}{6.83 \times 10^7} (2 \ln \frac{\Phi_1^*}{\Phi_o}) \]
(73)
Expanding in a power series
\[ s = \frac{F_1}{3.41 \times 10^7} \left[ \left( \frac{\Phi_1^*}{\Phi_0} - 1 \right) - \frac{1}{2} \left( \frac{\Phi_1^*}{\Phi_0} - 1 \right)^2 + \cdots \right] \]

\[ \approx \frac{F_1}{3.41 \times 10^7} \frac{(\Phi_1^* - \Phi_0)}{\Phi_0} \quad (74) \]

since \[ \left| \frac{\Phi_1^*}{\Phi_0} - 1 \right| < 0.2 \] in this work.

Hence

\[ \Phi_1 \approx \Phi_1^* + \frac{F_1}{5.11 \times 10^7} \frac{(\Phi_1^* - \Phi_0)}{\Phi_0} \Phi_1^{1/2} \]

\[ \approx \Phi_1^* + \frac{F_1}{5.11 \times 10^7} \frac{(\Phi_1^* - \Phi_0)}{\Phi_0} \Phi_1^{3/2} \quad (75) \]

Now \( F_1 \approx 3 \times 10^7 \) V/cm. Thus if \( \Phi_0 = 4.60 \) ev

then

\[ \Phi_1 \approx 1.06 \Phi_1^* - 0.27 \text{ ev} \quad (76) \]

and if \( \Phi_1^* = 4.00 \), \( \Phi_1 = 3.97 \) ev.

Therefore the evaluation of \( \Delta \phi = \Phi_1 - \Phi_0 \) by the comparison of the voltages required to obtain a given current should be accurate to better than 10%. However, this is based on the assumption that the emitting area remains constant. Examination of Figures 8 through 10 shows that the apparent emitting area did remain quite constant until the small crystallites began to form.

As a check on this assumption, the changes in work function during a similar experiment were obtained from the slopes of Fowler-Nordheim plots according to Equation 17. These are shown in Figure 12. It can be seen that both methods give
Figure 12. Change in work function measured from Fowler-Nordheim slopes
curves of the same character. However the magnitudes of the work function changes given by Equation 66 are smaller than those obtained from the Fowler-Nordheim plots. The difference is considerably larger than Equation 75 would predict, which indicates that large changes are occurring in the effective emitting area even though the apparent area remains the same. It was observed that the Fowler-Nordheim plots did not give very precise values for the work functions, primarily because of the error introduced in plotting a straight line through a small number of points with some scatter. This method also requires considerably more time for both the measurement and the processing of data. Since the single point method of Equation 66 was precise, quite reproducible, and much faster, most of the measurements were taken in this way. It was felt that the qualitative features of the changes in work function with heat treatment were shown better by this method.

Figure 13 shows the $\Delta \varphi$-T behavior for an emitter with a small dose of ethylene (less than a monolayer). The dosing was stopped before any darkening of the emission pattern was observed. The interesting feature of the curve is the peak in the region from 100° to 400 °K. Figure 11 also indicated a small peak in this region but it was not nearly so pronounced.

If the filament was heated to about 50 °K during dosing, it was possible to obtain a sharp boundary between the covered and uncovered portions of the tip. This behavior is shown in
Figure 13. Change in work function with flash temperature for a light dose of ethylene
the series of photographs in Figure 14. As the tip was heated to higher temperatures, the boundary showed no tendency to move, indicating that the adsorbed ethylene was quite immobile on the surface. Finally at about 600 °K the boundary was no longer visible because the work functions of the covered and uncovered areas were the same.

Under certain conditions during the flow experiments, rather unusual boundary migration was observed. A typical sequence is shown in Figure 15. The emitter was held at 77 °K and the pressure of ethylene flowing through the tube was 10^{-7} mm Hg. The filament was flashed to 2200 °K to clean it, then allowed to cool. Twenty seconds after the flash (which was about the time required for the filament to reach 77 °K) the sequence was photographed. Bright corners around the edge of the central 100 plane were observed which soon grew together to form a square. The bright square spread rapidly over the surface, eventually meeting other squares from the other 100 planes. These squares then slowly closed in around the close-packed 111 planes. Soon after the emitter became completely engulfed, small bright doublets scattered randomly over the tip began to appear and vanish again. The photograph does not completely resolve them, but each of the spots in Figure 15f was really a doublet shaped like an opposed pair of semicircles. The doublets could be observed to flicker, increase or decrease the intensity in discrete steps and
Figure 14a. An emitter showing Figure 14b. After heating a boundary between covered and bare areas 14a to 127 °K

Figure 14c. After heating to 297 °K

Figure 14d. After heating to 383 °K

Figure 14e. After heating to 468 °K

Figure 14f. After heating to 553 °K
Figure 15a. An emission pattern showing the onset of boundary diffusion in a flow experiment $T = 77\, ^\circ\text{K}, P = 10^{-7}\, \text{mm Hg}$

Figure 15b. After 15 seconds the boundary forms a square

Figure 15c. After 45 seconds

Figure 15d. After 1 minute the boundary is closing in around the 111 planes

Figure 15e. After 1.5 minutes

Figure 15f. After 2 minutes doublets appear
occasionally spin rapidly. The number of doublets grew with time, and eventually began to pile up toward the apex of the tip. This "piling up" appeared to be a field migration since it could be reduced by lowering the applied voltage.

Similar doublets have been observed by other workers with oxygen (46), and with larger organic molecules such as phthalocyanine (47). Melmed and Müller have shown fairly conclusively that small clumps of two or three phthalocyanine molecules can give rise to such patterns. Rose (48) has shown theoretically that if single molecules are adsorbed on small protrusions on the surface of a field emitter, the magnification can be enhanced enough to allow them to be resolved.

The nature of the bright squares is not known. The application of a strong electric field appeared to be necessary for the phenomenon to occur. The conditions of pressure, temperature and field were so critical that it was not possible to determine whether the process involved adsorption directly or was a field-induced reaction of previously adsorbed ethylene.

The doublets, on the other hand, were easily obtained whenever an excess of ethylene was adsorbed. Again, the process appeared to involve the field, for increasing the voltage caused the number of doublets to increase, but the additional doublets remained after the field was reduced again. At 4 °K when an excessive dose had been applied to the tip so that
the emission was greatly reduced (see Figure 16b), increasing the field caused small clumps of doublets to grow at various spots on the surface. If the field was maintained, the clumps grew in size and number, and migrated toward the apex of the tip, forming intensely emitting areas. Unless the field was immediately reduced, arcing occurred and the emitter was destroyed.

Adsorption of acetylene

Figures 16, 17, 18 and 19 show the emission patterns from an iridium emitter at 4 °K with adsorbed acetylene. The experiments were carried out in the same way as those with ethylene. Some differences in the patterns were noticeable. At low temperatures the acetylene appeared to increase the emission over slightly more of the surface than did the ethylene. The pattern for the acetylene covered emitter heated to 72 °K was, however, nearly identical to that for the heavily covered emitter at 77 °K in the ethylene flow system, Figure 15e. As the emitter was heated, the work function increased, as with the ethylene covered surface. A sharp decrease in emission from the 110 planes was observed above 400 °K. The maximum work function occurred after the filament was heated to 725 °K, which was about the temperature of the ethylene maximum. Above that temperature the emitting areas appeared granular, crystallites developed and finally large
Figure 16a. Clean iridium

Figure 16b. The emitter of 16a after dosing at 4 °K

Figure 16c. After heating to 72 °K

\[ \Delta \varphi = -0.24 \text{ ev} \]

Figure 16d. After heating to 129 °K

\[ \Delta \varphi = -0.60 \text{ ev} \]

Figure 16e. After heating to 316 °K

\[ \Delta \varphi = -0.58 \text{ ev} \]

Figure 16f. After heating to 410 °K

\[ \Delta \varphi = -0.54 \text{ ev} \]
Figure 17a. The emitter of 16f after heating to 550 °K
\[ \Delta \varphi = -0.32 \text{ ev} \]

Figure 17b. After heating to 644 °K
\[ \Delta \varphi = -0.09 \text{ ev} \]

Figure 17c. After heating to 737 °K
\[ \Delta \varphi = +0.02 \text{ ev} \]

Figure 17d. After heating to 831 °K
\[ \Delta \varphi = -0.08 \text{ ev} \]

Figure 17e. After heating to 1159 °K
\[ \Delta \varphi = -0.27 \text{ ev} \]

Figure 17f. After heating to 1252 °K
\[ \Delta \varphi = -0.33 \text{ ev} \]
Figure 18a. The emitter of 17f after heating to 1346 °K
\[ \Delta \varphi = -0.37 \text{ ev} \]

Figure 18b. After heating to 1440 °K

Figure 18c. After heating to 1533 °K

Figure 18d. After heating to 1720 °K

Figure 18e. Emission from iridium showing a boundary between bare surface and adsorbed C₂H₂

Figure 18f. After heating the emitter of 18e to 129 °K
Figure 19a. After heating the emitter of 18f to 222 °K

Figure 19b. After heating to 316 °K

Figure 19c. After heating to 410 °K

Figure 19d. After heating to 597 °K
clumps of crystallites became localized all around the periphery of the 110 regions. With ethylene, the clumps became prominent along the border between the 110 and 111 planes but did not surround the 110 region. When extremely large amounts of acetylene were heated above 1200 °K the emission patterns were indistinguishable from those using ethylene (see Figure 10c).

If the acetylene was added to an emitter held above 50 °K, boundaries were obtained between covered and uncovered portions of the emitter. When such tips were heated, no boundary motion was observed. Thus for acetylene as well as ethylene, the adsorbed species appeared to be immobile, at least below 600 °K. The effect of heating a tip with a boundary is shown in Figures 18 and 19.

The change in work function with flash temperature for an emitter with adsorbed acetylene is shown in Figure 20. The curve shows much the same type of behavior as was shown with ethylene except for the lack of a peak at 250-300 °K. The initial decrease is somewhat greater and the maximum is slightly lower than for ethylene.

It should be noted that these work function changes for both ethylene and acetylene were highly reproducible. Eight different emitters were studied with adsorbed ethylene and three with acetylene. In all cases the behavior was as indicated. For the same initial dose of ethylene (or acetylene)
Figure 20. Change in work function with flash temperature for acetylene on iridium
any two emitters gave almost identical work function changes.

It was observed that after six or seven desorption experiments with acetylene had been carried out on an emitter, the work function of the bare surface began to decrease and could not be increased by cleaning flashes. The emission pattern appeared to be that of a clean surface, yet the work function dropped to about 4.1 ev. This was probably due to diffusion of carbon into the lattice. When this decrease was detected, the emitter was discarded.

Adsorption of ethane

The change in work function caused by the adsorption of ethane is shown in Figure 21. The experimental procedure was the same as with ethylene and acetylene. The emission patterns were identical to those from an emitter covered with a light dose of ethylene. Yet the work function changed in a somewhat different manner from those observed with ethylene or acetylene.

Adsorption of hydrogen

To study the adsorption of hydrogen using a FEM at 4 °K it was necessary to use a different method for dosing the emitter. Klein (49) has observed that hydrogen has an appreciable vapor pressure at 4 °K, perhaps as high as $10^{-6}$ mm Hg. Therefore one cannot rely on condensing all the hydrogen on a cold finger. The gas source which was used
Figure 21. Change in work function with flash temperature for ethane on iridium
consisted of a spiral of 5 mil zirconium wire. The microscope was filled with a few millimeters pressure of hydrogen and the zirconium wire was heated electrically to a dull red glow to form zirconium hydride. Then the tube was evacuated and placed in the helium cryostat. This source was not entirely satisfactory, for after a few dosings the hydrogen pressure in the tube became quite noticeable.

The change in work function for a hydrogen covered emitter flashed at various temperatures is shown in Figure 22. This curve is qualitatively similar to that observed for hydrogen on nickel (39).

Experiments were also conducted with hydrogen in a flow system. It was observed that if hydrogen at a pressure of $6 \times 10^{-8}$ mm Hg was allowed to adsorb on an emitter at 300 °K, a decrease in emission occurred. However, if the emitter was held at 77 °K an initial decrease in emission was followed by a slight increase. When the filament was then heated the process was reversed. As the filament temperature was slowly raised from 77° to 250 °K, the emission decreased; above 250 °K the emission increased. A decrease in work function following an initial increase has also been observed for hydrogen on tungsten field emitters (50) and evaporated films (51) and on nickel films (52).

**Kinetic studies**

A very striking feature of the adsorption of both ethylene and acetylene was the sharp increase in work function
Figure 22. Change in work function with flash temperature for hydrogen on iridium.
occurring between 350° and 700 °K. Separate flash filament studies (see the following section) indicated this increase was due to a desorption process. Therefore experiments were conducted to determine the time and temperature dependence of the changes in $\phi$.

The experiments were carried out with a FEM immersed in liquid helium. The emitter was given a fixed dose of adsorbate at 4 °K, then warmed to 200 °K to allow the work function to come to a standard value. Then the filament was flashed to a given temperature between 400 and 700 °K for varying periods. At the end of each heating period, the filament was cooled to 4 °K and the work function was determined by measuring the voltage required for $10^{-6}$ amps emission. As a result of the heating, the work function increased rapidly at first, then more slowly. When the work function showed little change with further heating, the flash temperature was increased. In this manner the dependence of $\Delta \phi$ upon $t$ at various temperatures was determined over the temperature range in which the desorption occurred.

In the analysis of these data it is assumed that the extreme values of work function correspond to the presence of two different species on the surface which, for the moment, we shall not attempt to characterize. At the minimum value of $\phi$ the surface is completely covered with species I; at the maximum it is completely covered with II. The change in $\phi$
is due to the reaction

\[ \text{I} \xrightarrow{k} \text{II} + \text{gas} \quad (77) \]

At the minimum \( \varphi \)

\[ \Delta \varphi = \Delta \varphi_\text{I} \quad (78) \]

and

\[ \Theta_\text{I} = 1 \]

where \( \Theta_\text{I} \) is the fraction of the adsorbed material which is present as \( \text{I} \). At some higher value of \( \varphi \) it is assumed, following Equation 22, that

\[ \Delta \varphi = \Delta \varphi_\text{I} \Theta_\text{I} + \Delta \varphi_\text{II} \Theta_\text{II} \quad (79) \]

Then since \( \Theta_\text{I} + \Theta_\text{II} = 1 \),

\[ \Delta \varphi = \Delta \varphi_\text{I} \Theta_\text{I} + \Delta \varphi_\text{II} (1 - \Theta_\text{I}) \quad (80) \]

or

\[ \Theta_\text{I} = \frac{\Delta \varphi - \Delta \varphi_\text{II}}{\Delta \varphi_\text{I} - \Delta \varphi_\text{II}} \quad (81a)** \]

From the experimental data it was evident that the rate of the desorption depended strongly on \( \Theta_\text{I} \) as well as on \( T \). Therefore it was assumed that the activation energy for the desorption depended linearly on \( \Theta_\text{I} \). This type of behavior has been frequently observed and is the physical basis for the Temkin isotherm (53). Now we suppose that the rate of

**Note that this equation also holds for \( \Delta \varphi^* \) if \( \Delta \varphi = a\Delta \varphi^* + b \) according to Equations 75 and 76. Thus

\[ \Theta_\text{I} = \frac{\Delta \varphi^* - \Delta \varphi_{\text{II}}^*}{\Delta \varphi_{\text{I}}^* - \Delta \varphi_{\text{II}}^*} \quad (81b) \]
desorption is given by the Polanyi-Wigner equation

\[ -\frac{d\theta}{dt} = v\theta \exp \left[ -\frac{\Delta H}{RT} \right] \]  

and letting \( \Delta H = \Delta H_0 - \alpha \theta \), where \( \theta = \theta_1 \)

\[ -\frac{d\theta}{dt} = v\theta \exp \left[ \frac{(\alpha \theta - \Delta H_0)/RT}{v^2} \right] \]  

Separating variables and integrating,

\[ \int_{\theta_1}^{\theta_2} \frac{e^{-\alpha \theta/RT}}{\theta} d\theta = -vt \exp \left[ -\frac{\Delta H_0}{RT} \right] \]  

To evaluate the integral on the left, we let \( x = \frac{\alpha \theta}{RT} \)

Then

\[ \int_{\theta_1}^{\theta_2} \frac{e^{-\alpha \theta/RT}}{\theta} d\theta = \int_{x_1}^{x_2} \frac{e^{-x}}{x} dx = E_i(x_1) - E_i(x_2) \]  

where \( E_i(x) = \int_{x}^{\infty} \frac{e^{-t}}{t} dt \), \( x > 0 \).

Tables of \( E_i(x) \), the exponential integral, are available (54). Therefore, the time \( t \) required for the coverage to go from \( \theta_1 \) to \( \theta_2 \) at a temperature \( T \) can be calculated from

\[ t = \frac{1}{v} \left[ E_i\left(\alpha \theta_2/RT\right) - E_i(\alpha \theta_1/RT) \right] \exp \left[ \frac{\Delta H_0}{RT} \right] \]  

This equation gives the \( t-\theta \) relationship in terms of three parameters: \( v \), \( \Delta H_0 \), and \( \alpha \). It was possible to fit the experimental data quite closely by choosing various values of these parameters. Figures 23 and 24 present the dependence of \( \theta \) upon \( t \) at various flash temperatures for ethylene and acetylene desorption respectively. The points are experimen-
Figure 23. Time dependence of work function at various flash temperatures for ethylene on iridium.
Figure 24. Time dependence of work function at various flash temperatures for acetylene on iridium.
tal; the curves were calculated from Equation 16. $v$ was set equal to $kT/h$ which was equivalent to assuming zero entropy of activation. It was quite simple to find unique values of $\Delta H_0$ and $\alpha$ to fit the data for any given desorption experiment. The value of $\Delta H_0$ determined the $\Theta$ at which the curve began to break, while the value of $\alpha$ determined how sharp the break was. $\Delta H_0$ and $\alpha$ were determined to better than +1 kcal/mole by the accuracy of the fit. Table 1 lists the actual temperatures of the various desorption experiments shown in Figures 23 and 24 and the value of $\Delta H_0$ and $\alpha$ used to fit the data.

The fact that $\Delta H_0$ for ethylene was nearly constant over the entire temperature range indicates that the correct value for $v$ was used. At any one temperature $T_1$, $v$ and $\Delta H_0$ are not both uniquely determined by the data since the same curve is obtained using values $v'$ and $\Delta H_0'$ such that

$$v \exp[-\Delta H_o/RT_1] = v' \exp[-\Delta H'_o/RT_1]$$

(87)

If $v$ and $\Delta H_0$ are the correct values, at some other temperature $T_2$

$$v \exp[-\Delta H_o/RT_2] = v' \exp[-\Delta H'_o/RT_2]$$

(88)

If $v'$ is held constant at $T_1$ and $T_2$ it can easily be shown that

$$\frac{\Delta H'_o - \Delta H_o}{T_1} = \frac{\Delta H''_o - \Delta H_o}{T_2}$$

(89)
Table 1. Parameters used for expressing desorption data

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Temperature</th>
<th>$\Delta H_o$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>468 °K</td>
<td>40 kcal</td>
<td>10 kcal</td>
</tr>
<tr>
<td>1'</td>
<td>468</td>
<td>39.5</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>477</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>494</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>502</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>553</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>5'</td>
<td>553</td>
<td>39.5</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>579</td>
<td>41.2</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>587</td>
<td>41.2</td>
<td>12</td>
</tr>
<tr>
<td>8</td>
<td>638</td>
<td>42.5</td>
<td>20</td>
</tr>
<tr>
<td>Acetylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>462</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>B</td>
<td>501</td>
<td>48.5</td>
<td>18</td>
</tr>
<tr>
<td>C</td>
<td>540</td>
<td>49</td>
<td>18</td>
</tr>
<tr>
<td>D</td>
<td>579</td>
<td>47.5</td>
<td>16</td>
</tr>
<tr>
<td>E</td>
<td>617</td>
<td>47.4</td>
<td>16</td>
</tr>
<tr>
<td>F</td>
<td>656</td>
<td>46.5</td>
<td>14</td>
</tr>
<tr>
<td>G</td>
<td>695</td>
<td>46.5</td>
<td>14</td>
</tr>
</tbody>
</table>

so that $\Delta H_o' \neq \Delta H_o''$

Thus if the correct value of $v$ is chosen, $\Delta H_o$ is independent of the temperature. From the data for ethylene it was possible to determine that $v = kT/h$ was correct within an order of magnitude.

A similar argument was used to support the assumption that the desorption was first order in $\theta$. Figure 23 shows two curves marked 1' and 5' which were calculated for a second-order desorption. The values of $\Delta H_o$ and $\alpha$ for these
curves were chosen in such a way that \( l' \) gave a good fit with the data at 468 °K. Then \( 5' \) was calculated for 553 °K using these same values. The figure indicates that it was not possible to fit both sets of data with single values of \( \Delta H_0 \) and \( \alpha \).

For many systems, the activation energy for desorption does not vary linearly with coverage. There are, however, valid theoretical grounds for supposing that the activation energy changes linearly with the work function of the surface (55, 56). If the surface dipoles are regarded as forming a continuous double layer, the energy of adsorption is lowered by the work required to place an additional charge in the double layer. Boudart (55) has suggested that the activation energy for desorption will thus be decreased by an amount

\[
\Delta H_0 - \Delta H = \frac{1}{2} \Delta \phi
\]  

Equation 81a can be written

\[
\theta_I = A\Delta \phi + B
\]

Using this expression, Equation 82 becomes

\[
-A \frac{d\Delta \phi}{dt} = v(A\Delta \phi + B)\exp\left[\frac{(-\Delta H_0 + \alpha B + \alpha A\Delta \phi)}{RT}\right]
\]

Thus it can be seen that we have really assumed only that \( \Delta H \) varies linearly with \( \Delta \phi \). Furthermore we see that

\[
\Delta H(\Delta \phi_{II}) - \Delta H(\Delta \phi_I) = \alpha = \frac{1}{2}(\Delta \phi_{II} - \Delta \phi_I)
\]
from Equation 90. From Figure 12 for ethylene \( \frac{1}{2}(\Delta \varphi_{II} - \Delta \varphi_I) = .42 \text{ ev} = 9.6 \text{ kcal/mole} \). From Table 1, \( \alpha = 10 \text{ kcal/mole} \). It should be noted that other linear relationships between \( \Delta \mathcal{H} \) and \( \Delta \varphi \) have been proposed (57) so that the agreement found here is not completely conclusive.

It was not possible to fit the experimental data over the entire range of \( \Theta \) and \( T \) with single values of \( \Delta \mathcal{H}_0 \) and \( \alpha \). A plot of the variation of \( \Delta \mathcal{H} \) with \( \Theta \) was constructed using the values of \( \Delta \mathcal{H}_0 \) and \( \alpha \) found for various increments of \( \Theta \) and is shown in Figure 25. It can be seen that the deviations from linearity are small. These deviations may reflect real variations in \( \Delta \mathcal{H} \). In the case of acetylene, there is a uniform deviation which could be caused by the neglect of a small entropy of activation.

The sharp increase in \( \varphi \) which occurred with ethane on iridium at about 100 °K was studied in a similar fashion. From the rate of change of \( \varphi \) with \( T \) the activation energy \( \Delta \mathcal{H}_0 \) for the process was found to be about 10 kcal/mole while \( \alpha \), the change in \( \Delta \mathcal{H} \), was 3 kcal/mole.

**Flash Desorption Experiments**

**Desorption of hydrogen**

Flash filament experiments with hydrogen were carried out to obtain quantitative information about the number of adsorption sites and the desorption energy. It was immediately
Figure 25. Variation of the activation energy for desorption with coverage
apparent that some modification of the previously described analysis of flash filament data was necessary. In that treatment it was specified that the pumping of all gas sinks was negligible. It was observed, however, that hydrogen was rapidly pumped by the hot ionization gauge filament. That this was not caused by ion pumping was shown by the constant pumping speed at widely varying ion currents. Even when the reaction cell and gauge were completely isolated from the pumps by ground glass valves, a burst of hydrogen from the flash filament was pumped away at about 2 l/sec.

To analyze this situation we proceed in the following manner. Letting $N$ be the total number of molecules in the gas phase, Equation 29 can be written

$$\frac{dN}{dt} + N \frac{S}{V} = F$$

Integrating,

$$\Delta N = N(t) - N(t_0) = e^{-\frac{St}{V}} \int_{t_0}^{t} F e^{-\frac{St}{V}} dt$$

where $t_0$ is the time at which desorption becomes apparent.

If we consider a second order desorption, from Equations 30, 32 and 35

$$F = A n^2 [X(t) + C]$$

where $C = \frac{\gamma}{\alpha} e^{\alpha t_0}$. Equation 35 can be used to change the variable of integration in Equation 95 to $X(t)$. Then
\[ \Delta N = n_0^2 \exp \left( \frac{-S T}{V} - \frac{S}{V \alpha} \right) \int_0^{X(t_1)} \frac{(X + C)}{(1 + n_0 X)^2} \, dX \]  \hspace{1cm} (97)

where \( \tau = t_1 - t_0 \). Upon changing variables again to \( y = X + C \),

\[ \Delta N = n_0 \exp \left( \frac{-S T}{V} - \frac{S}{V \alpha} \right) \int_C^{C'} \frac{e^{\alpha \tau}}{C} \frac{S}{y \alpha} \frac{dy}{(1 + n_0 + C + y)^2} \] \hspace{1cm} (98)

Equation 98 is of the form

\[ \int_C^{C'} \frac{y^2}{(y + 8)^2} \, dy = y^2 \int_C^{C'} \frac{dy}{(y + 8)^2} \] \hspace{1cm} (99)

by the mean-value theorem of calculus, with \( C \leq y \leq C' \).

Hence

\[ \Delta N = n_0 \left[ \frac{n_0 X}{1 + n_0 X} \right] \exp \left[ \frac{-S}{V} (t_1 - \xi) \right] \] \hspace{1cm} (100)

where \( t_0 \leq \xi \leq t_1 \).

This equation is easily interpreted. In the absence of pumping it follows from Equation 35 that

\[ \frac{\Delta N}{\Delta N_{\text{max}}} = \frac{n_0 - n}{n_0} = \frac{n_0 X}{n_0 X + 1} \]

or

\[ \Delta N = n_0 \left[ \frac{n_0 X}{n_0 X + 1} \right] \] \hspace{1cm} (101)

Thus the \( \Delta N \) of Equation 100 can be seen to be the total number of molecules desorbed reduced by a pumping correction factor \( \exp \left[ -\frac{S}{V} (t_1 - \xi) \right] \). For low pumping speeds and rapid
desorption rates this correction is small. A reasonably good approximation is then to take $\xi = (t_1 - t_0)/2$. Then

$$\frac{\Delta N}{\Delta N_C} = \frac{\Delta P}{\Delta P_C} = \exp\left[ -\frac{S}{2V} (t_1 + t_0) \right]$$

(102)

where the subscript indicates the quantity corrected for pumping. $X(t)$ can then be calculated from Equation 37 using corrected $\Delta P$ values. By choosing various other values for $\xi$ the approximation was found to affect $\Delta H$ only slightly while rendering the values of $n_0$ and $v$ uncertain by about 10% (which is less than the uncertainty due to filament end effects and ion gauge calibration).

A typical hydrogen desorption curve is shown in Figure 26. The curve is the recorded pressure measured by the ion gauge as the filament was flashed. The pressure change was corrected for pumping in the manner described and $X(T)$ was calculated for both first and second order processes. The plot of log $X$ vs. $1/T$ is shown in Figure 27. From the linearity of the second order plot it was concluded that the hydrogen desorption was a second order process and thus the hydrogen was adsorbed as atoms. The activation energy for desorption was determined from the slope of the second order plot to be 17 kcal/mole. From Equation 38, $v$ was then found to be $5.6 \times 10^{-4}$ cm$^2$ molecules$^{-1}$ sec$^{-1}$.

As a check on the method for correcting for pumping, the pressure in the system was calculated from Equation 100 using
Figure 26. Flash desorption of hydrogen adsorbed at 300 °K on iridium
Figure 27. Analysis of pressure-temperature data for hydrogen on iridium by first and second order kinetics.

Second order kinetics:
- $\Delta H = 17.0 \text{ Kcal/MOLE}$
- $n = 60 \times 10^{12} \text{ molecules/cm}^2$

First order kinetics:

Logarithmic plot against $1/T \times 10^3$. 

$\log \left( \frac{n_0 - n}{n_0} \right)$ vs $1/T \times 10^3$.
the values obtained for \( n_0 \) and \( \Delta H \). The calculated points are shown on the measured curve of Figure 26.

At values of \( n_0 \) less than \( 80 \times 10^{12} \) molecules/cm\(^2\) the second order plots of \( \log X \) were linear with a constant slope indicating that \( \Delta H \) was independent of \( n_0 \). When \( n_0 \) was larger than \( 80 \times 10^{12} \), deviations from linearity became apparent and the slopes decreased indicating a lowering of the activation energy. We have already indicated that the analysis of the desorption data is based on the assumption that \( \Delta H \) is independent of \( n \). Thus it was only possible to obtain qualitative information about \( \Delta H \) at higher coverages. \( \Delta H \) decreased to about 13 kcal/mole as \( n_0 \) increased to \( 180 \times 10^{12} \) molecules/cm\(^2\).

The maximum value of \( n_0 \) at a given pressure and temperature was measured by increasing the adsorption period until \( n_0 \) was constant. With the filament at 300 °K and a pressure of \( 2 \times 10^{-8} \) mm Hg the maximum amount adsorbed was \( 100 \times 10^{12} \) molecules/cm\(^2\), increasing to \( 180 \times 10^{12} \) at \( 6 \times 10^{-7} \) mm Hg.

In the initial stages of this work it was occasionally observed that the desorption spectrum revealed two peaks, one at 400 °K and the other at about 600 °K. The peak at 600 °K increased in magnitude while that at 400 °K decreased as the adsorption time was increased. Hickmott and Ehrlich (19) observed a similar phenomenon with hydrogen on tungsten. With the aid of an omegatron mass spectrometer they were able to characterize the high temperature peak as CO produced by the
ion gauge filament. Becker et al. (58) have discussed in detail the production of CO from tungsten filaments. They were able to remove carbon completely from a tungsten filament by heating it to 2400 °K in oxygen at 10⁻⁶ mm Hg for 24 hours. This treatment was tried with the ion gauge used in the hydrogen desorption experiments. Afterward, no peak was observed at 600 °K even after a 12 hour adsorption period. Thus it seems very likely that this peak was due to CO.

When filaments were cooled to 77 °K during the adsorption of hydrogen, two peaks were again observed upon flashing. Figure 28 shows such desorption spectra at two different heating rates. It is evident that rapid pumping of the gas from both peaks was occurring. Since this type of spectrum was observed after the ion gauge had been treated to remove carbon and since pumping was observed it seems nearly certain that both peaks were due to hydrogen.

This indicated the hydrogen was adsorbed in two distinct forms with different binding energies. Attempts were made to analyze the low temperature peak in the manner which has been described. It was of considerable interest to determine from the desorption kinetics whether the low temperature form was dissociated to atoms. However, the low temperature form (which we shall designate the α form) was desorbed with a continually varying activation energy so that the method of analysis was not applicable. From a comparison with the high
Figure 28. Flash desorption of hydrogen from iridium initially at 77 °K
temperature from \( \text{the } \beta \text{ form} \) it was estimated that the desorption energy was about 11 kcal/mole.

Figure 28b shows that the \( \alpha \)-hydrogen was adsorbed much more slowly than the \( \beta \) form, but in larger amounts. At \( 4 \times 10^{-8} \text{ mm Hg} \) about \( 190 \times 10^{12} \text{ molecules/cm}^2 \) was adsorbed in the \( \alpha \) form while about half as much was adsorbed in the \( \beta \) form at saturation. Hickmott (20) observed two forms of adsorbed hydrogen on tungsten but the \( \alpha \) form was never adsorbed in amounts comparable to the \( \beta \) form. Hickmott felt that the \( \alpha \) species was molecular hydrogen.

**Desorption of ethylene**

Qualitative experiments on the flash desorption of ethylene were conducted. Samples of the observed desorption spectra are shown in Figure 29. The spectrum of Figure 29a was obtained after adsorption at 300 °K. Two important features can be observed. First, the desorption occurred in the temperature range 375°-600 °K which was exactly the range where the marked increase in work function was observed on ethylene covered field emitters. The second feature is the rapid pumping of the desorbed gas which occurred. Once again, the only pump was the hot ion gauge filament. Separate experiments where small bursts of ethylene were added to the reaction vessel failed to show any pumping. It must therefore be concluded that the desorbed gas was almost entirely hydrogen.
Figure 29. Flash desorption of ethylene from iridium initially at:
  a. 300 °K, b. 77 °K, c. 77°K
Figures 29b and 29c show desorption spectra from a filament which was cooled to 77 °K during adsorption. Besides the small peak at 100 °K another new feature is the break in the curve which is barely resolved at 350 °K. Again, the apparent pumping indicates the desorbed material was almost completely hydrogen. At slower filament heating rates it was possible to obtain somewhat better resolution of the two peaks. It was concluded that hydrogen was desorbed from ethylene-covered iridium in two steps of nearly equal magnitude. The amount of hydrogen desorbed after exposure to ethylene at 10^{-7} \text{ mm Hg} was about 200 \times 10^{12} \text{ molecules/cm}^2.
DISCUSSION

The following sequence of reactions is proposed to explain the experimental observations for the adsorption of hydrogen, ethane, ethylene and acetylene on iridium:

a. $H_2 + 2* \rightleftharpoons 2H^*$
b. $2^* + C_2H_6(g) \rightleftharpoons H_2^*-CH_3 + H^*$
c. $2^* + H_2C-CH_3 \rightleftharpoons H_2^*-CH_2^* + H^*$
d. $2^* + C_2H_4(g) \rightarrow H_2^*-CH_2$
e. $4^* + H_2C-CH_2 \rightleftharpoons H_2^*-CH_2 + 2H^*$
f. $4^* + C_2H_2(g) \rightarrow H_2^*-C-H$
g. $2^* + H_2C-CH \rightleftharpoons H^*-CH + 2H^*$

The stars denote adsorption sites on the metal surface which are not necessarily identical. The proposed structures of absorbed hydrocarbons which the symbols above represent are:

- $H_2C-CH_3$
- $CH_2-CH_2$
- $CHCH$
These structures are all assumed to be similar to that of the ethane molecule. Molecular models have been constructed and are shown on a 100 iridium crystal face in Figure 30. The symbol (\( \bullet - \bullet \)) denotes pairs of carbon atoms covalently bonded to surface iridium atoms, which probably form an iridium carbide. The existence of these reactions has been inferred from observed work function changes and measurements of desorption rates at various temperatures.

In order to draw conclusions about reaction rates from work function changes, it has been necessary to use the assumption given by Equation 79; namely, the net surface potential on a surface covered with two adsorbed species is the algebraic sum of the surface potentials produced by each of the two species alone. When the individual dipoles are weak, electrostatic interactions are small and the assumption is probably valid.

From the observed temperature dependence of these reactions kinetic mechanisms are proposed. The evidence for these reactions and the proposed mechanisms are presented in the following discussion.

Adsorption of Hydrogen

\[
H_2 \rightleftharpoons 2H^*
\]

Hydrogen is adsorbed dissociatively on iridium at 300 °K since the kinetics of desorption are second order. Moreover, the hydrogen atoms on the surface must be quite mobile since
a. $H_2C-CH_3$

b. $H_2C-CH_2$

c. $HC-CH$

Figure 30. Models for adsorbed hydrocarbons on iridium
the pre-exponential factor in the desorption rate constant is 5.6 \times 10^{-4} \text{ cm}^2 \text{ molecules}^{-1} \text{ sec}^{-1}. If the hydrogen atoms behaved as a two dimensional gas on the surface and desorption occurred whenever two atoms with sufficient energy collided, the pre-exponential factor would be the total number of collisions in unit time. In that case it can be shown that

\[ \nu = \sigma \left( \frac{\pi kT}{m} \right)^{\frac{1}{2}} \]

where \( \sigma \) is the hard sphere collision diameter of the hydrogen atom. If \( \sigma \) is taken as 1 Å then \( \nu = 3 \times 10^{-3} \text{ cm}^2 \text{ molecule}^{-1} \text{ sec}^{-1} \) at 400 °K, in reasonably close agreement with the measured value.

From the measured activation energy for desorption, the energy of adsorption of hydrogen can be calculated since adsorption occurs with no activation energy. (This is indicated by the increased work function observed on adsorption even at 4 °K.) The binding energy for a hydrogen atom is then

\[ E_{\text{M-H}} = \frac{1}{2}(E_{\text{H-H}} + \Delta H) = \frac{1}{2}(103 + 17) = 60 \text{ kcal/mole} \]

where \( E_{\text{H-H}} \) is the dissociation energy of the hydrogen molecule.

It is often instructive to consider the amount of adsorption in terms of the number of adsorbed atoms per surface metal atom. The number of surface atoms can be estimated if the crystallographic orientation of the surface is known. With iridium the wire axis was known to have a \( \langle 100 \rangle \) orientation; thus from Figure 6c the surface consisted largely
of 100 and 110 areas. The density of atoms on a 100 face is $1.36 \times 10^{15}$ atoms/cm$^2$; on a 110 face it is $0.96 \times 10^{15}$ atoms/cm$^2$. Since the 100 planes are somewhat more developed than the 110 we can take $1.20 \times 10^{15}$ atoms/cm$^2$ as a good approximate value. Then one hydrogen atom was adsorbed for every eight surface iridium atoms before the adsorption energy began to decrease noticeably. The maximum coverage observed at 300 °K and $5 \times 10^{-7}$ mm Hg was one hydrogen for every three iridium atoms.

The adsorption of hydrogen at 77 °K occurs in two distinct binding states. The tightly bound hydrogen in the β state is identical with hydrogen adsorbed at 300 °K. Adsorption at 77 °K into the β state is quite rapid; however the amount adsorbed in this state is about two-thirds of the amount adsorbed at 300 °K. Adsorption into the α state is much slower, with the β state being filled first. The maximum amount adsorbed in the α state at 77° and $4 \times 10^{-8}$ mm Hg was one hydrogen atom per two iridium atoms. Recent work has been reported with hydrogen on molybdenum showing a similar behavior (59). Hydrogen is more strongly adsorbed on molybdenum, so that the desorption peaks occur at 350 °K and 550 °K respectively. With hydrogen on iridium peaks occur at 285 °K and 410 °K.

It is very interesting to note the correlation between the work function changes observed for hydrogen adsorption in
the flow system and the formation of the α-state. At 300 °K adsorbed hydrogen only increased the work function. At 77 °K an initial increase of about 0.3 ev was observed, followed by a decrease of about 0.2 ev. Warming the emitter reversed the process with the work function reaching a maximum at about 250 °K, then slowly decreasing to the clean value. Thus the β hydrogen increases the work function while the α hydrogen lowers it.

Sachtler and Dorgelo (50) observed similar work function changes with hydrogen on a tungsten emitter. They attributed the lowered work function to the adsorption of hydrogen molecules, which were supposedly bound by weak three-center bonds. Their analysis was qualitative and not very convincing.

Eischens and Pliskin (60) studied the infrared spectra of hydrogen and deuterium adsorbed on supported platinum. They also found evidence of two types of adsorption, each of which gave distinctive absorption bands. From the fact that no new bands were observed when hydrogen and deuterium were simultaneously adsorbed, they deduced that the weakly bound form must also be present as atoms. They suggested that the strongly bound hydrogen atoms were situated between the surface atoms and held by shared bonds. The weakly bound atoms were located above the surface, each singly bound to a platinum atom. They were able to present convincing arguments
for this model from the analysis of the observed absorption lines.

de Boer (57) has suggested that the adsorption of hydrogen may take place with the formation of hydrogen atoms located slightly below the surface. If these hydrogen atoms then donate electrons to the metal, a negative surface double layer can result, giving an increased work function. Furthermore, the electrons donated to the metal could cause the increased conductivity observed when hydrogen is adsorbed on thin films of platinum and nickel (61).

It would be desirable to determine the kinetic order of the desorption of the α hydrogen to afford a test for these theories. The present experiments were not able to do this conclusively, although there were some indications that the process was second order. These experiments did show that the change in character of adsorbed hydrogen at low temperatures does not arise through a gradual decrease in adsorption energy with coverage, but rather through an entirely different adsorption mechanism. This mechanism probably involves a different set of adsorption sites. A careful study of the sticking coefficients for the two states at various temperatures would undoubtedly increase our understanding of these adsorption processes.

Adsorption of Ethane

\[ C_2H_6(gas) \rightleftharpoons (C_2H_6)_{phys.~ads} \]
Ethane appears to be only weakly adsorbed on iridium. From observations of the rate of desorption measured by the work function change, the activation energy is 10 kcal/mole and shows some dependence on coverage. Although it is difficult to make a clear-cut distinction on the basis of energy, both the desorption energy and its dependence on coverage are somewhat high for physical adsorption.

Not all of the ethane is removed by desorption at 150 °K. A small residue which is not removed until 1800 °K remains, giving an increased work function. This residue gives emission patterns which are identical with those obtained using small amounts of ethylene. Thus some dehydrogenation of the ethane seems to occur even below 150 °K. We can therefore characterize the adsorption of ethane at low temperatures as primarily physical, but with some chemical interaction causing a small amount of dehydrogenation. Wright et al. (62) studied the dehydrogenation of ethane on nickel films and found evidence of considerable hydrogen evolution at 273 °K.

**Adsorption of Ethylene**

\[
C_2H_4(\text{gas}) + 2^* \rightarrow H_2C=CH_2
\]

\[
\text{H}_2\text{C}-\text{CH}_2 + 4^* \rightarrow \text{HC}^*\text{CH} + 2^*\]
Adsorption and initial dehydrogenation

Ethylene is adsorbed on iridium at 4 °K causing a decreased work function. When deposited on the surface in excessive amounts, the ethylene increases the work function by forming dielectric layers of physically adsorbed material; these are removed by heating to 50 °K. At 4 °K, the ethylene is only weakly bound which is indicated by the nearly complete spreading of the adsorbed material which occurs. By 50 °K, the ethylene is strongly bound since adsorption at that temperature produces sharp boundaries which do not migrate below 600 °K.

Above 200 °K the work function rises to a small peak at 250 °K and then decreases over the range 250-400 °K. The flash desorption of ethylene adsorbed at 77 °K indicates that a desorption process begins at about 250 °K with a barely resolved peak at 350 °K followed by another peak at 550 °K. The evolved material is rapidly pumped by the hot ion gauge filament in a manner characteristic only of hydrogen. When corrected for pumping, the magnitudes of the pressure peaks at 350 °K and 550 °K are about equal, indicating that the hydrogen is desorbed from the ethylene covered surface in two equal steps. No desorption peaks are observed at higher temperatures; therefore all the hydrogen must be desorbed in these
two steps since it is extremely unlikely that any hydrogen remains on the surface above 1500 °K. From this evidence we postulate the reactions

\[
\begin{align*}
H_2C-CH_2 & \rightarrow H^*C-CH + H_2 \\
H-C-CH & \rightarrow (C-C) + H_2
\end{align*}
\]

There is a close correspondence between the temperature range for the initial desorption at 350 °K and the range over which hydrogen is desorbed from iridium. This leads one to suspect that the rate controlling step in this reaction may simply be the desorption of adsorbed hydrogen, a surface dissociation having already taken place. Over the temperature range of this desorption, the work function is decreasing. It was observed that the desorption of hydrogen from iridium lowers the work function since the β hydrogen causes a negative dipole layer to form. It seems reasonable then that the decrease in work function observed from 250 °K to 400 °K is caused by the desorption of hydrogen atoms from the metal.

The hydrogen atoms are formed from the decomposition of adsorbed ethylene. It seems rather doubtful that ethylene adsorbed at 4 °K would undergo very much dissociation. Thus the dissociation must occur at some higher temperature and should be indicated by an increase in the work function due to the formation of negative dipoles. This process probably
accounts for the rise in \( \phi \) observed from 200–500 °K. We now write these reactions as

\[
\text{H}_2\text{C-CH}_2 + 4^* \xrightarrow{250 \degree K} \text{H}^*\text{C-CH} + 2^* \\
2^* \xrightarrow{350 \degree K} \text{H}_2 + 2^*
\]

From comparison of Figures 11 and 13 we see that the peak at 250 °K is much more pronounced when the initial amount of ethylene adsorbed is small. This behavior can be explained if we assume that the rate of the dehydrogenation reaction above depends on coverage,

\[
\frac{d[H]}{dt} = k[\ast]^4 [\text{H}_2\ast\ast\ast\ast\text{C-CH}_2]
\]

A smaller number of empty sites will certainly decrease the rate. Thus high initial ethylene concentrations reduce the amount of dehydrogenation, which is indicated by the smaller work function peak.

In principle it should be possible to measure the time-temperature dependence of the work function in the region around the first peak. The kinetic behavior of the work function below 250° should furnish information about the activation energy for the dehydrogenation step at various coverages. The kinetics of the work function decrease above 250 °K should agree with the kinetics for hydrogen desorption. In practice such measurements were not feasible because of the relatively small work function changes involved.
We have inferred the progress of surface dehydrogenation from the increase in work function which was attributed to the adsorbed hydrogen atoms, but we have ignored the possibility that the associatively adsorbed ethylene, $\text{H}_2\text{C-C}_2\text{H}_2$, may have a dipole moment different from that of the dissociatively adsorbed form, $\text{HC-CH}$. There is both experimental and theoretical evidence for both forms having nearly the same moment. It seems reasonable that adsorbed acetylene at low temperatures should have the structure $\text{HC-C}_2\text{H}$ since dehydrogenation does not occur until above 450 °K. It has been shown experimentally that the work function change produced by acetylene was only slightly larger than that produced by ethylene at temperatures low enough to avoid dehydrogenation. Let us assume that both species have an ethane-like structure on the surface; then viewed along the C-C axis

\[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{H} \\
& \quad * & \quad \text{C} & \quad * & \quad * \\
\text{H} & \quad \text{C} & \quad * & \quad * & \quad * \\
& \quad * & \quad \text{C} & \quad * & \quad * 
\end{align*}
\]

for adsorbed ethylene and acetylene respectively. If we let $\mu_H$ denote the C-H bond moment and $\mu_M$ denote the C-M bond moment, the net moment normal to the surface for an ethylene molecule is

\[
\bar{\mu} = 2 \cos 19^\circ 28' \left[ 2\mu_H \cos 60^\circ - \mu_M \right] = 1.886 \left[ \mu_H - \mu_M \right]
\]

That for adsorbed acetylene is

\[
\bar{\mu} = 2 \cos 19^\circ 28' \left[ \mu_H - 2\mu_M \cos 60^\circ \right] = 1.886 \left[ \mu_H - \mu_M \right]
\]
The factor \( \cos 19°28' \) corrects for the fact that all the bonds make an angle of \( 19°28' \) with a plane normal to the molecular axis. Thus both species should cause nearly the same work function change. Of course, such a calculation is very approximate and does not take into account the variations in configuration that may result from adsorption on different crystal planes.

**Final dehydrogenation of ethylene**

Let us now consider the surface reactions occurring between 450 °K and 700 °K. We have already shown that desorption of hydrogen occurs in this region with an accompanying increase in the work function. In the preceding section we argued that the desorption of hydrogen occurring between 250 °K and 350 °K should cause a decrease in \( \varphi \). How can we then reconcile that argument with the observed large increase occurring during the second desorption step? An important fact to consider is that this second step occurs in a temperature range where hydrogen is completely desorbed from the bare metal. It is not likely that the hydrogen atom concentration on the ethylene covered surface will be high enough in this region to affect the work function at all. The observed effects must be entirely due to the removal of hydrogen atoms from the adsorbed acetylenic complex. If we suppose that the completely dehydrogenated species forms a surface
carbide, it is not surprising to observe an increased $\phi$, since
the metal-carbon bond would be expected to have the greatest
electron density on the carbon atom. However, it is not
possible to characterize this surface carbide completely from
the available information.

From the observed kinetics of the work function change
in this region it is possible to differentiate between various
dehydrogenation mechanisms. Let us first consider

$$HC-\text{CH} \xrightleftharpoons{K} (C-C) + 2H_2$$

$\theta$ \hspace{1cm} 1-\theta

$$2H \xrightarrow{k} H_2$$

i.e. the rate controlling step is the evolution of hydrogen
from the bare surface. Then letting $\theta$ denote the fraction of
acetylenic complex remaining,

$$-\frac{d\theta}{dt} = \frac{d[H_2]}{dt} = k[H]^2$$

But

$$[H]^2 = k \frac{\theta}{1-\theta}$$

Thus

$$-\frac{d\theta}{dt} = kK \frac{\theta}{1-\theta}$$

In the early stages of dehydrogenation $\theta$ is still large and
the rate would not be first order. In this region the ob-
erved rate followed first order kinetics quite closely and we
can thus eliminate this mechanism.
The rate determining step must then involve the rupture of C-H bonds. Three mechanisms for this are possible. In the first we suppose that the two hydrogen atoms on the adsorbed molecule combine directly and desorb. Schematically,

\[ \begin{align*}
\text{H} & \quad \text{H} \\
\text{C-C} & \quad \xrightarrow{k_1} \quad \text{H-H} \\
\quad \text{\( \Theta \)} & \quad \quad \text{\( \quad \)} \\
& \quad \quad \text{\( 1-\Theta \)} \\
\end{align*} \]

Then for this process

\[ -\frac{d\Theta}{dt} = \frac{d[H_2]}{dt} = k_1 \Theta \]

and the order agrees with the observed kinetics. The second possibility is that the C-H bonds are simultaneously broken with the hydrogen atoms becoming adsorbed on the metal. In this temperature range the adsorbed hydrogen atoms rapidly recombine and are evolved from the metal. Thus

\[ \begin{align*}
\text{HC-CH} & \quad \xrightarrow{k_2} \quad (\text{C-C}) + 2\text{H} \\
\quad \Theta & \quad \quad \text{\( \quad \)} \\
& \quad \quad \text{\( 1-\Theta \)} \\
\end{align*} \]

\[ 2\text{H} \quad \xrightarrow{k} \quad \text{H}_2 \quad \text{fast} \]

Since the rate of removal of \( \text{H} \) is very rapid, the concentration will at all times be small, and we can assume that a steady state is attained. Then

\[ \frac{d[H]}{dt} = 0 = \frac{1}{2}k_2 \Theta - \frac{1}{2}k[H]^2 \]

Again
\[-\frac{\text{d}e}{\text{d}t} = \frac{\text{d}[H_2]}{\text{d}t} = k[H]^2\]

Hence

\[-\frac{\text{d}e}{\text{d}t} = k_2 \theta\]
again in agreement with the observed order.

From the reaction order, these last two mechanisms are indistinguishable. There will be some difference in the activation energies for the two processes. The first process appears quite similar to the desorption of hydrogen from a graphite surface and might be expected to have a similar activation energy. The activation energy for the second mechanism will probably depend to some degree on the strength of metal-hydrogen interactions. Simple bond energy calculations illustrate this point clearly. The energy of a C-H bond is about 98 kcal/mole (63). The H-H bond energy is 103 kcal/mole. A rough estimate of the activation energy for the direct desorption of hydrogen is then the difference in the bond energies,

\[\Delta E \sim 2(98 - 103) = 93 \text{ kcal/mole}\]

The bond energy of adsorbed hydrogen was found to be 60 kcal/mole. Then the activation energy for desorption via hydrogen-metal bonding is approximately

\[\Delta E \sim 2(98 - 60) = 76 \text{ kcal/mole}\]

This illustrates the reduction in the height of the energy
barrier obtained from metal-hydrogen interactions. If this second mechanism is operative, a decrease in activation energy should be observed for this reaction on metals with a larger hydrogen bond energy. Hydrogen is adsorbed on nickel with a bond energy of about 67 kcal/mole. From the experiments of Jenkins and Rideal (64), ethylene is completely dehydrogenated on nickel at 450 °K, indicating a lower activation energy than observed with iridium.

A final mechanism to consider is one in which hydrogen atoms are lost one at a time from the acetylenic complex. The method which was used to follow the rate measured only the concentration of positive dipoles. Each C-H bond forms one such dipole, and if the hydrogen atoms are lost individually, these dipoles act independently. Effectively

\[
\begin{align*}
\text{H} & \xrightarrow{k_3} \text{C} + \text{H}^* \\
\theta & \rightarrow 1 - \theta
\end{align*}
\]

where the arrow indicates the polarity of the dipole. Then assuming a steady concentration of adsorbed hydrogen as before it can be shown that

\[
-\frac{d\theta}{dt} = k_3 \theta
\]

But now the activation energy is just that required to break one C-H bond. Approximately, \( \Delta E \approx 98-60 = 38 \text{ kcal/mole} \), which is very close to the value of 42 kcal/mole observed for ethylene. Thus a mechanism involving surface dehydrogenation
followed by rapid desorption of hydrogen from the metal surface seems indicated.

It is rather curious that such a difference in dehydrogenation rate is observed for the first and second pair of hydrogen atoms in an ethylene molecule. A possible explanation is that $\text{H}_2\text{C-CH}_2$ is fairly free to oscillate about the single carbon-metal bonds allowing hydrogen atoms to come close to the metal surface. The acetylenic complex $\text{HC-CH}_2$, on the other hand, is not free to rotate because of the additional pair of bonds. The remaining hydrogen atoms are held away from the surface, and can only approach when the carbon-metal bonds become weakened by thermal vibrations. The strength of the carbon-metal bonding is demonstrated by the absence of surface migration even at 600 °K which is illustrated in Figure 14.

**Adsorption of ethylene on other metals**

At this point it is useful to examine what is already known about the adsorption of ethylene on clean metal surfaces. Beeck (65) studied the adsorption of ethylene on evaporated films of various metals including nickel, platinum, and rhodium, which are all fairly similar to iridium. On nickel he found that one molecule of ethylene required twice as many sites as one molecule of hydrogen and four times as many as a molecule of CO. Furthermore, the adsorbed ethylene completely covered the surface; no hydrogen or CO could be
adsorbed. From the very reasonable assumption that CO required one site and H₂ two sites, he concluded that ethylene required four adsorption sites. This was explained by assuming that ethylene initially dissociated on the surface to form adsorbed acetylene, occupying two sites, and two adsorbed hydrogen atoms. The hydrogen atoms would react with excess ethylene to form ethane which did not adsorb. Eventually all the hydrogen atoms were removed and more ethylene was adsorbed with a final ratio of one adsorbed ethylene for every two sites. Thus Beeck proposed

\[ C_2H_4(g) + 4* \rightarrow HC = CH + 2H \]

Jenkins and Rideal (64) performed similar experiments and were able to show further that the rate of ethane production when gaseous ethylene was added to a nickel film covered with adsorbed ethylene was the same as when the ethylene was added to a hydrogen covered film. They also found that when a surface which had been treated with an excess of ethylene to remove all adsorbed hydrogen atoms was heated to 450 °K hydrogen was evolved. The amount of hydrogen was equal to the amount of ethylene which had been adsorbed. Thus ethylene adsorbed on nickel at 300 °K apparently loses half its hydrogen upon adsorption and the other half upon heating above 450 °K.

Eischens and Pliskin (66) studied the infrared absorption spectra of ethylene adsorbed on a supported nickel catalyst.
While this can scarcely be considered a clean surface, their method of preparation was sufficiently rigorous to remove most of the surface contamination. Their observations indicated that ethylene adsorbed on bare nickel at 300 °K did indeed lose hydrogen. However, the spectra indicated that the carbon atoms were saturated even though the number of hydrogen atoms per carbon was low. This suggested that either bonds were formed between adjacent ethylene molecules or that the carbon atoms were bound to more than one nickel atom.

When ethylene was allowed to adsorb on nickel which was previously covered with hydrogen the spectrum indicated that dissociation did not occur. The C-H stretching bands indicated the carbon atoms were saturated while a H-C-H bending band showed that each carbon retained two hydrogen atoms. These results suggest a surface equilibrium

\[ 4* + H_2C - CH_2 \rightleftharpoons \star \star \star HC-CH + 2H \star \star \]

This equilibrium is also indicated by the results obtained when hydrogen was added to ethylene adsorbed on bare nickel. The spectrum indicated that conversion to the associatively adsorbed form occurred. By controlling the hydrogen pressure, the reaction could be driven in either direction. The addition of hydrogen to associatively adsorbed ethylene caused a shift in the absorption bands which was attributed to adsorbed ethyl radicals, hence

\[ \star H + H_2C-CH_2 \rightleftharpoons \star H_2C-CH_3 \]
When ethane was adsorbed on bare nickel, a spectrum was obtained which was identical to that for ethylene on bare nickel; thus extensive dehydrogenation occurred. When ethane was allowed to contact hydrogen covered nickel, no evidence for adsorption could be obtained.

Adsorption of Acetylene

\[ C_2H_2 + 4^* \rightarrow H^*_C - CH \]

\[ HC-CH \rightleftharpoons (C-C) + 2H^* \]

The adsorption of acetylene on iridium appears very similar to that of ethylene. The chief difference is the absence of the peak in the work function curve at 250 °K observed with ethylene. This indicates clearly that acetylene is adsorbed on iridium without dissociation and thus is evidence for a structure \( H^*_C - CH \). This also supports the proposal that the peak observed for ethylene is due to the loss of two hydrogen atoms.

Above 450 °K acetylene undergoes a dehydrogenation exactly like that observed with ethylene. The reaction kinetics are very nearly the same as those for ethylene.

The small differences in the emission patterns which are observed for ethylene and acetylene are attributed to differences in the amount of adsorption occurring at 4 °K. Acetylene appears to adsorb more extensively on the low index planes than does ethylene. This is not surprising if
acetylene forms more bonds with the surface.

Above 700 °K surfaces covered with ethylene and acetylene both show a decreasing work function which appears to be caused by carbon dissolving into the metal lattice. Above 1200 °K small crystallites begin to appear on the surface which are probably graphitic carbon. As the surface is heated higher, more and more carbon difuses back out of the lattice, forming small clumps of crystallites. Finally around 1800 °K the carbon is evaporated from the surface.

A number of additional experiments would be useful in testing these ideas. If both ethylene and hydrogen could be added to a field emitter from separate sources it should be possible to reverse the surface dehydrogenation process. Duplication of these experiments on other metals would indicate how changing adsorption energies alter the kinetics of surface dehydrogenation. Calorimetric measurements of adsorption heats at various temperatures should show interesting effects. Mass spectrometric analysis of the desorbed gas would verify the presence of hydrogen and determine the extent, if any, to which hydrocarbons may be evolved.

Flash desorption experiments were not attempted with ethane and acetylene. The flash desorption of ethane after adsorption at various temperatures should furnish information about the kinetics of dehydrogenation. The flash desorption of acetylene would indicate the amount of adsorption which
could be compared with that for ethylene. Observation of the emission during the adsorption of acetylene in a FEM at various flow pressures would indicate whether any dehydrogenation occurs on a bare surface at temperatures above 4 °K. When ethylene was studied in this way, the work function initially increased, indicating decomposition. From the proposed reaction scheme this would not be expected with acetylene.

Applications to Catalysis

This work was not intended as a study of catalytic hydrogenation. Nevertheless, the surface reactions which are believed to occur with ethylene and acetylene certainly have a bearing on hydrogenation. The surface reactions which have been proposed have all been suggested (67) in various reaction schemes for hydrogenation yet no one seems to have considered to any extent the conditions under which the various reactions become important. Probably a large factor in the apparent confusion on the subject is the lack of good well-defined experimental results. Most of the results which are available have been obtained from poorly characterized surfaces at relatively high pressures. The small amount of work which has been done on relatively clean surfaces has not been carried out over a wide enough temperature range to show the changes in mechanism caused by the surface reactions we have observed.
SUMMARY

The adsorption of ethane, ethylene, acetylene and hydrogen on clean iridium surfaces was studied by field emission electron microscopy and flash-filament desorption techniques.

The field emission microscope was so constructed that it was possible to vary the temperature of the iridium emitter precisely from 4 °K to 1700 °K by means of a liquid helium cryostat and controlled electrical heating. It was therefore possible to follow changes in emission patterns and work functions resulting from time and temperature dependent surface reactions. To avoid complications from field dependent reactions, all work functions were measured at 4 °K. Distinctive changes in emission patterns and work functions resulted from the adsorption of hydrogen, ethane, ethylene and acetylene on iridium; further marked changes, which were both time and temperature dependent, resulted when the metal with adsorbed gas was heated for various times at various temperatures.

These changes are interpreted in terms of adsorption, surface reaction and desorption processes. Work function changes are assumed to be linearly related to surface concentrations of adsorbed species; the validity of this assumption is discussed. Kinetic mechanisms are then presented which suffice to represent semi-quantitatively the observed work function changes with all species studied, including their time and temperature dependence. Activation energies thus
calculated are shown to agree well with those estimated from bond energy calculations.

Flash-filament desorption experiments with hydrogen and ethylene verified the existence of desorption reactions and provided values for the activation energies. The results were consistent with the proposed mechanisms.

It was found that ethane is only weakly adsorbed on iridium, with desorption occurring near 100 °K. Some decomposition occurs, leaving ethylene and hydrogen on the surface. Ethylene is strongly adsorbed with dissociation, the extent of which depends on coverage. Desorption of hydrogen from an ethylene covered surface occurs in two equal steps. The rate of the first is determined by the rate of hydrogen desorption from the metal, that of the second by rupture of carbon-hydrogen bonds. Acetylene is strongly adsorbed and appears similar to ethylene after the first dehydrogenation step.

The results of these studies indicate the necessity for studying catalytic hydrogenation reactions over a broad temperature range in order to observe the effects of these surface dehydrogenation processes.
BIBLIOGRAPHY


ACKNOWLEDGEMENT

It is a great pleasure to acknowledge the help and encouragement of Professor R. S. Hansen. The stimulating discussions and lectures of Professor Hansen have been the main source of the author's understanding of surface chemistry.