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SCHOOL OF ENGINEERING

THESIS

WRIGHT-PATTERSON AIR FORCE BASE, OHIO

THE THEORY OF SURFACE IONIZATION
AND ITS
APPLICATION TO ION PROPULSION

THESIS

Presented to the Faculty of the School of Engineering
of the Institute of Technology
Air University
in Partial Fulfillment of the
Requirements for the Degree of
Master of Science

By

Donald D. Mueller, B.S. M.E.

1st Lt

USAF

Graduate Astronautics

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Preface

This paper represents an attempt to condense and summarize all the published information available on the subject of surface ionization. I have attempted to present the material in a language which does not presuppose an extensive background in solid state physics or quantum mechanics.

I first became aware of the need for such a paper after reading a thesis by Battle and Davis (GA/Phys/60-1, 2) on the design of an ion engine. Desiring more information on the theory of ion sources, I found myself sifting through forty years of literature on the subject (most of it out of date). I soon realized that, while a great deal has been written about surface ionization, the parameters of interest to an ion rocket designer (mainly critical temperature) have been all but ignored in the older literature. In this paper I have concentrated on those aspects of the theory which are most important to ion propulsion.

The bibliography which follows the text is not complete since it does not include many of the papers in the Soviet literature. It does, however, include most of the important work which has been published in the English language and represents the work of the most active researchers in this field. It should be an invaluable aid to anyone doing research on surface ionization.

I wish to thank my thesis adviser, Dr. William L. Lehmann, for his enlightening discussions, particularly on the quantum mechanical aspects of the theory. I am also indebted to J. M. Ferguson and R. E. Hunter of the Electric and Advanced Propulsion Branch of the Aeronautical Systems

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Division, Wright-Patterson Air Force Base, and to Dr. G. Kuskevics of the Flight Propulsion Laboratory, General Electric Company, for their helpful comments. Finally, I am grateful to my wife, Pat, for her invaluable assistance in proofreading and assembling the final manuscript.

Donald D. Mueller

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Abstract

This paper is a critical review of approximately 100 references on surface ionization and ion propulsion. The Saha-Langmuir equation for a homogeneous surface with no adsorbed atoms is derived. The effects of a heterogeneous surface, adsorbed atoms, and electric fields are discussed in detail. After a brief description of experimental techniques and the extent to which the theory is confirmed by experiment, the application of the theory to ion propulsion is examined. Particular emphasis is placed on the porous plug ionizer. The areas in which future research should be directed are indicated.

THE THEORY OF SURFACE IONIZATION
AND ITS
APPLICATION TO ION PROPULSION

I. Introduction

The purpose of this paper is to summarize the present knowledge on the subject of surface ionization and to discuss the application of the theory to ion propulsion.

Many papers have been published on the subject of surface ionization and closely related phenomena. However, many of the basic laws underlying the theory are still not clearly understood. Very few reviews of surface ionization theory have appeared recently (Ref 50, 105), and many of the older ones are now out of date. Rapid advances in the investigation of this complex subject have prompted the writing of this paper in the hope that a critical review of previous results may assist further work.

Background Information

Surface ionization refers to the production of positive (or negative) ions at the surface of a heated body from which atoms or molecules are evaporating. The phenomenon of surface ionization was first noted in 1923 by Dr. Irving Langmuir and his co-workers at the General Electric Research Laboratories (Ref 44, 54). Langmuir was studying the chemical reactions that occur when various gases are introduced into evacuated glass bulbs containing heated tungsten filaments. He unexpectedly made the discovery

that small amounts of alkali metal vapor introduced into the bulb caused positive alkali ions to be emitted from the incandescent tungsten filament.

From considerations of thermodynamic equilibrium and electron emission laws, Langmuir was able to derive a theoretical expression for the ratio of positive ions to neutral atoms which are given off from a heated metal surface. This expression is the well known Saha-Langmuir equation and is derived in the first section of this paper.

In experiments using cesium and hot tungsten filaments, Langmuir was able to confirm his theory quantitatively. Further work by Ives (Ref 44), Becker (Ref 11), Killian (Ref 49), Copely and Phipps (Ref 19), and others resulted in the further development and confirmation of the theory for elements other than cesium and tungsten.

At the time this early work was being done there was no immediate practical application for surface ionization and so, after about 1935, only a handful of physicists in this country and the Soviet Union actively pursued the subject. Surface ionization was relegated to the role of a mere scientific curiosity until very recently, when it was proposed as an efficient source of ions for electrostatic propulsion.

At the present time more than a dozen industrial research organizations and universities have government contracts to study surface ionization with the express purpose of applying it to ion propulsion (Ref 39). Obviously, many scientists, engineers, and military contracting officers who had no previous knowledge of or experience with the theory, will now be required to devise, conduct, and evaluate experiments involving surface ionization.

Plan and Scope of this Paper

The paper begins with a derivation of the Saha-Langmuir equation which is found to hold for homogeneous surfaces which are free from adsorbed atoms.

Owing to the heterogeneous nature of actual metal surfaces, the work function is not uniform and the effect of this patchy surface is to change the value of some of the parameters in the Saha-Langmuir equation. This fact plays an important part in the interpretation of experimental results.

Since adsorbed films of foreign atoms play a major role in determining the minimum temperature at which surface ionization can occur, considerable space is devoted to a discussion of the mechanism of adsorption on solids and its effect on the electron work function. A discussion of the effect of electric fields on the work function concludes the section on theory.

The next part of the paper is devoted to a brief description of experimental techniques and a discussion of the extent to which the theory is confirmed by experiment.

Finally, the application of the theory to ion propulsion is discussed. Particular emphasis is placed on the porous ionizer and some general conclusions concerning ionization on porous surfaces are stated.

While several authors (principally Dobretsov in the Soviet Union) have treated surface ionization from the standpoint of wave mechanics, such an approach is beyond the scope of this paper. Only a brief mention of the quantum mechanical method, as it applies to the energy state of an adsorbed atom, is made in the section on adsorption.

This paper is based on a survey of approximately 100 references on surface ionization, ion propulsion, and related subjects dating back to

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1923. The appended bibliography lists all important papers since 1923 which have come to the author's attention and which bear on the fields covered by this review. In addition, Kuskevics' paper (Ref 50) contains an extensive bibliography of 250 references, and the excellent article by Zandberg and Ionov (Ref 105) contains a valuable list of 113 references, mostly from the Soviet literature.

II. Theory

In order to intelligently discuss the results of experiments, it is necessary to first examine in detail the analytical expressions derived by Langmuir (Ref 54, 60) to describe surface ionization.

Derivation of the Saha-Langmuir Equation

One of the parameters of interest in surface ionization is the ionization coefficient, α , which is defined as the ratio of the number of positive ions to the number of neutral atoms emitted per unit of time per unit of surface area.

$$\alpha = \frac{\nu_p}{\nu_a} \quad (1)$$

where

ν_p = Flux of positive ions from unit surface area

ν_a = Flux of neutral atoms from unit surface area.

Also of interest is the fraction of incident atoms that is ionized by the heated metal surface. This is called the ionization efficiency, β , and can be obtained directly from α by the relationship

$$\beta = \frac{\nu_p}{\nu_p + \nu_a} = \frac{\frac{\nu_p}{\nu_a}}{\frac{\nu_p}{\nu_a} + 1} = \frac{\alpha}{\alpha + 1} \quad (2)$$

The ionization coefficient, α , is given by the Saha-Langmuir equation

$$\alpha = \frac{v_p}{v_a} = \frac{g_p}{g_a} \exp\left[\frac{(\phi - V_i)e}{kT}\right] \quad (3)$$

where

g_p = Statistical weight of the ionic state

g_a = Statistical weight of the atomic state

ϕ = Thermionic work function of the surface

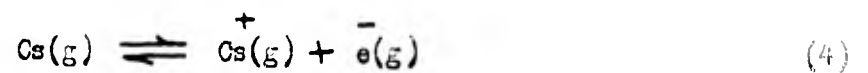
V_i = Ionization potential

e = Electronic charge

k = Boltzmann's constant

T = Temperature of the surface.

This expression can be obtained by considering the chemical equilibrium which exists between gaseous atoms, ions, and electrons. We can write the following equation for the dissociation of cesium, say:



where (g) signifies the gaseous phase.

The equilibrium concentration of atoms, ions, and electrons is given by

$$K_m = \frac{n_p n_e}{n_a} = \frac{g_p g_e}{g_a} \left[\frac{2\pi m k T}{h^2} \right]^{3/2} \exp\left(\frac{-V_i e}{kT}\right) \quad (5)$$

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where

$n_p =$ Number of ions per cm^3

$n_e =$ Number of electrons per cm^3

$n_a =$ Number of neutral atoms per cm^3

$g_e =$ Statistical weight of an electron = 2

$m =$ Mass of an electron

$h =$ Planck's constant.

This expression was first derived by Saha (Ref 83, 95) from considerations of statistical thermodynamics.

Equation (5) may be rearranged to give

$$\frac{n_p}{n_a} = \frac{K_m}{n_e} \quad (6)$$

The concentration of electrons near the surface of a heated metal can be obtained from thermionic emission laws and the relation

$$n_e = \frac{J}{e \bar{v}_x} \quad (7)$$

where J is the thermionic electron current density and \bar{v}_x is the average velocity of the electrons normal to the emitting surface. J is given by the well known Dushman equation for thermionic emission

$$J = g_e \left(\frac{2\pi m e k^2}{h^3} \right) T^2 \exp\left(\frac{-\phi e}{kT}\right) \quad (8)$$

Thermionic electrons are known to have a Maxwellian distribution of velocities characteristic of the temperature of the emitting surface

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(Ref 59:138,36). Hence, the average velocity normal to the surface can be calculated from kinetic theory to be

$$\bar{v}_x = \left(\frac{kT}{2\pi m} \right)^{1/2} \quad (9)$$

When equations (7), (8), and (9) are substituted into equations (5) and (6), we obtain equation (3), the Saha-Langmuir equation.

Because of the two possible spin orientations of the valence electron, the statistical weights of an alkali metal atom and ion are 2 and 1 respectively. Thus, for alkali atoms, the Saha-Langmuir equation becomes

$$\alpha = \frac{v_p}{v_a} = \frac{1}{2} \exp \left[\frac{(\phi - V_i)e}{kT} \right] \quad (10)$$

Figures 1 and 2 show theoretical curves for the ionization of several alkali metals on tungsten. These curves are based on equations (10) and (2).

It is well to consider the assumptions inherent in the derivation of equation (10) in order to determine its validity. These assumptions may be listed as follows:

1. Thermodynamic equilibrium exists between the ions, atoms, and electrons near the surface of the metal.
2. Ions, atoms, and electrons coming up to the surface are not specularly reflected by the surface.
3. The metal surface is homogeneous with a constant work function, ϕ .
4. The work function, ϕ , is not affected by the presence of adsorbed alkali atoms and ions on the surface.

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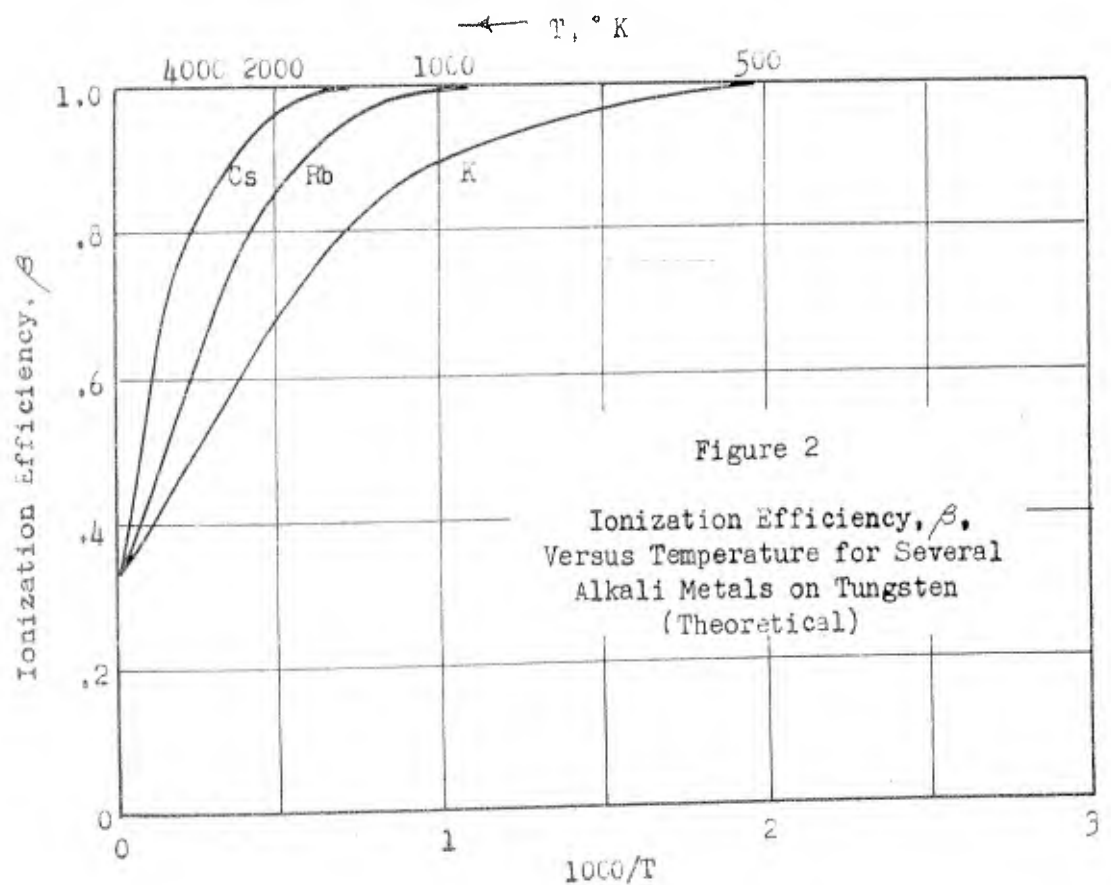
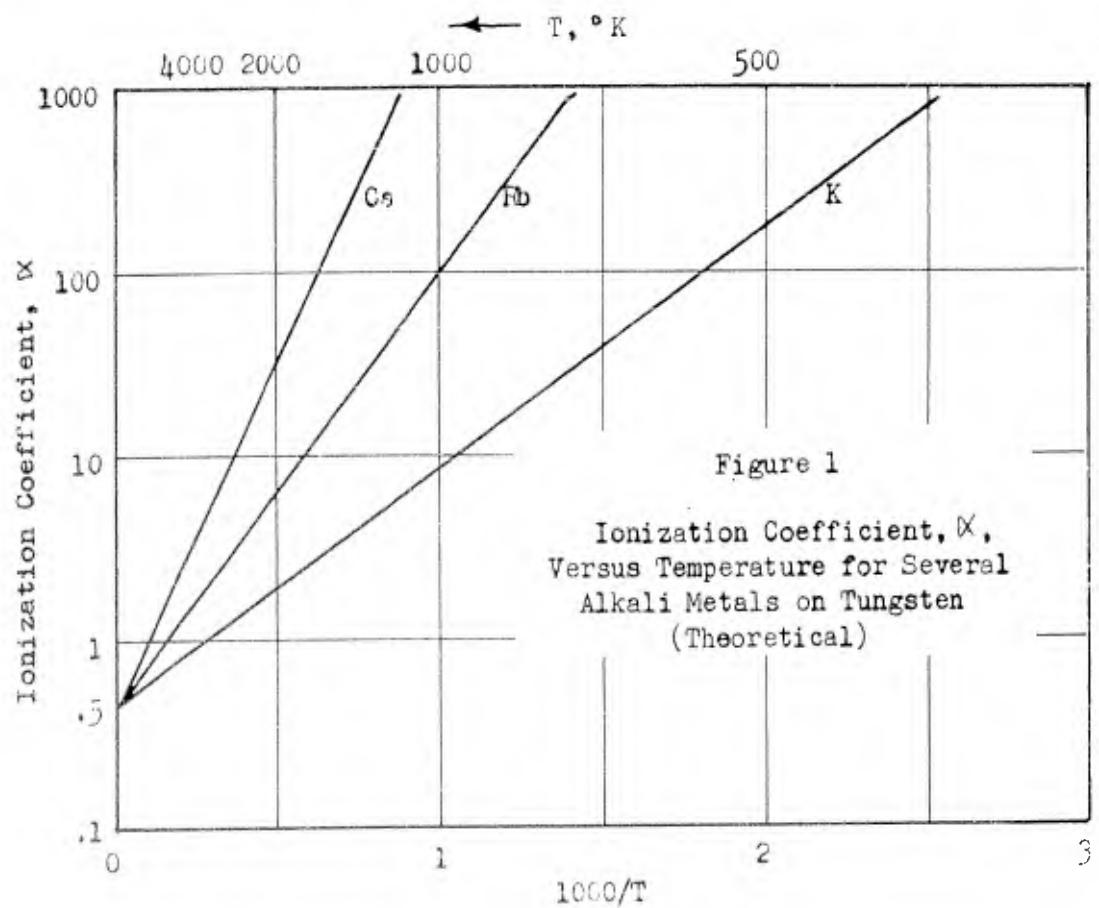
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Of these four assumptions, probably the first two come the closest to being correct. Experimental confirmation of equation (10) at high temperatures, where the adsorption of atoms on the surface can be neglected, indicates that equilibrium must, in fact, exist near the surface.

The problem of the reflection of ions and atoms has been studied by Copley and Phipps (Ref 19), and they have derived modified forms of the Saha-Langmuir equation to take this phenomenon into account. Taylor and Langmuir (Ref 97), however, measured a zero reflection coefficient for cesium atoms striking clean tungsten and concluded that, because of the strong attractive forces between a cesium ion and a tungsten surface, the reflection coefficient for ions was very likely also zero.

In the derivation of the Dushman equation for thermionic emission, it was assumed that every electron approaching the surface with sufficient energy to pass over the potential barrier was emitted. However, from considerations based on the application of wave mechanics, it can be shown that some of the electrons will be reflected at the boundary (Ref 27:466); but, if the potential barrier is not extremely steep, the reflection coefficient is very nearly zero.

Assumptions 3 and 4 are certainly not true in general, and so, we should not expect equation (10) to apply to patchy surfaces or at temperatures where adsorption becomes a factor.

Effect of a Patchy Surface

Recent thermionic emission studies on single crystals indicate that there is a wide variation in the work function for the different crystal

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faces of a metal (Ref 41,67). Table I lists typical values obtained from such experiments on tungsten single crystals. Since we are almost always concerned with surface ionization on a polycrystalline surface, it is necessary to examine what effect such a patchy surface has on the parameters α and β . The following analysis, due to Zemel (Ref 106), provides an answer to this question.

Table I

Variation of Electron Work Function for the Different Faces of a Tungsten Single Crystal

Miller Indices	Work Function, ϕ , ev
111	4.39
112	4.69
116	4.39
001	4.56
110	4.68

(From Ref 41:202)

If we assume that the surface is composed of patches with work function ϕ_k and fractional area f_k , it is a simple matter to show that the over-all ionization efficiency for the surface is

$$\beta = \sum_k \beta_k f_k \quad (11)$$

The ionization efficiency for each patch is obtained by substituting equation (3) into equation (2).

$$\beta = \left\{ 1 + \frac{q_a}{g_p} \exp \left[\frac{(\phi_k - v_i)e}{kT} \right] \right\}^{-1} \quad (12)$$

By making use of the relationship

$$\alpha = \frac{\beta}{1 - \beta} \quad (13)$$

and equations (11) and (12), the ionization coefficient for the entire surface can be written as

$$\alpha = \left\{ \left[\sum_k \frac{f_k}{1 + \frac{q_a}{g_p} \exp \left[\frac{(\phi_k - v_i)e}{kT} \right]} \right]^{-1} - 1 \right\}^{-1} \quad (14)$$

This expression is the modified Saha-Langmuir equation for a patchy surface. If only one term of the summation is taken, equation (14) reduces to equation (3).

The discussion of equation (14) will be deferred to a later section. Let it suffice to say here that the results of most experiments can only be explained in terms of this rather complicated expression.

Effects of Adsorption

Atoms of alkali metal vapor impinging on a heated metal surface condense and subsequently evaporate after coming to thermal equilibrium with the surface. Because of the time lag between condensation and evaporation there will be, at any time, a certain fraction of the surface covered by adsorbed atoms. This fraction depends on the rate at which atoms are

impinging on the surface and the rate at which they are evaporating. In general, if the temperature is low enough, the surface may become covered by a monatomic film of adsorbed atoms.

In the case of alkali metals on surfaces of high work function, the adsorbed atoms lose their valence electron and exist as ions. Because this layer of adsorbed ions has a profound effect on the work function of the underlying surface, it is necessary to consider the effects of adsorption on the phenomenon of surface ionization.

Types of Binding. Adsorption on solids is generally classified according to the type of binding force involved in holding the adsorbed atoms or molecules to the underlying surface. The three principal types of binding forces are covalent, ionic, and van der Waals.

Adsorption where covalent bonds are formed is sometimes called chemisorption, although, as Langmuir points out, "In the structure of matter there can be no fundamental distinction between chemical and physical forces." (Ref 58:60). Frequently the covalent bonding between adsorbed atoms and the solid is stronger than the cohesion of the solid; thus a large part of the oxygen adsorbed on charcoal can only be removed as oxides of carbon (Ref 1:253).

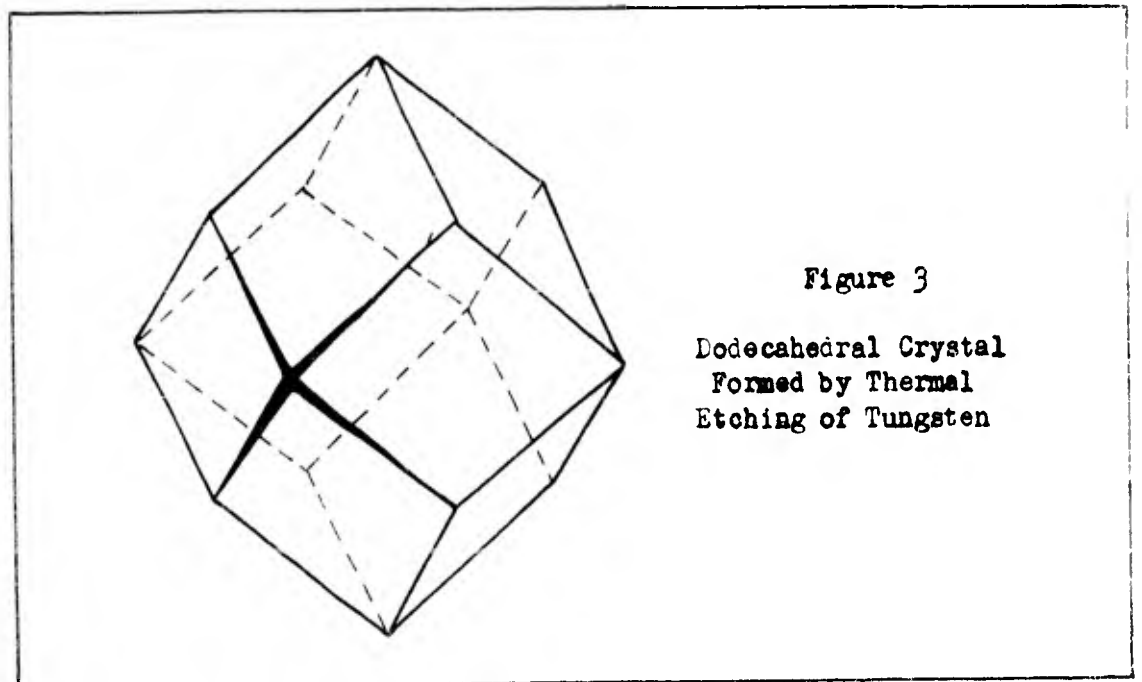
Adsorption of alkali metals on tungsten occurs through simple electrostatic forces. Because of the high work function of the tungsten and the low ionization potential of the alkali metals, the adsorbed atoms tend to lose their valence electron to the Fermi electron gas and become ions. These ions are then held to the underlying metal by coulomb attractive forces.

If the adsorption is of the van der Waals type, the molecules are not dissociated on the surface. Van der Waals attractive forces depend on the mutual polarizability of molecules and are usually considered to vary as the inverse seventh power of the distance between molecules. Because of the extremely short range nature of these forces, the molecules are more or less mobile in the adsorbed layer and can move along the surface. This motion, however, may be a series of activated hops from one place of low potential energy to another rather than a continuous motion such as exists in the three dimensions of a gas.

The Nature of an Adsorbed Film. The forces exerted by the underlying solid on adsorbed atoms or molecules tend to hold the molecules in definite positions fixed by the crystal lattice of the solid. Thus, we may consider that the solid is a type of checkerboard, containing a definite number of elementary spaces, each of which may accommodate an adsorbed molecule. Since these elementary sites correspond to places of minimum potential energy, we would expect that something analogous to an activation energy would be required to move a molecule from one elementary space to another. Hence, only those molecules possessing sufficient kinetic energy to pass over a potential barrier can succeed in hopping from one elementary space to an adjacent vacant space. This activation energy accounts for the surface mobility of adsorbed films at high temperatures and the disappearance of this mobility at low temperatures. In the case of cesium adsorbed on tungsten, the activation energy, as measured by Langmuir (Ref 62), is 0.61 electron volts.

In general, then, we may consider an adsorbed film on a solid as a two-dimensional crystalline gas, the crystalline character being imparted by the underlying lattice.

As an example, let us consider a tungsten surface which has been aged at a high temperature in a vacuum. Langmuir has shown that, after heating to 2900°K , a tungsten filament develops dodecahedral crystals in which only the (110) faces are exposed (Ref 58:324). This may be explained by the fact that tungsten has a body-centered cubic (BCC) crystal structure. In BCC crystals the (110) planes have the densest atomic packing and are the most widely separated; hence, the binding force between adjacent (110) planes is the weakest. When a BCC crystal is heated, thermal etching causes the (110) faces to grow at the expense of the other crystal faces. Since there are six (110) planes in BCC structures, dodecahedral crystals are formed as shown in figure 3.



The lattice constant of tungsten is 3.15 \AA and so there are 1.425×10^{15} tungsten atoms per cm^2 on a (110) face. Cesium also has a BCC structure but the lattice constant is 6.17 \AA , almost exactly double that of tungsten. Therefore in a complete monatomic layer of cesium on tungsten, the cesium atoms arrange themselves in a surface lattice identical with that of the underlying tungsten but with double the atomic spacing. Thus there is a 4 to 1 ratio of tungsten to cesium atoms in a complete adsorbed layer. This makes the surface concentration of a complete cesium film on tungsten 3.563×10^{14} atoms per cm^2 .

Of course, a random distribution of dodecahedral crystals results in an uneven surface whose actual area is greater than the equivalent area of a smooth surface. Langmuir determined experimentally that the number of cesium atoms per cm^2 of apparent surface was 4.80×10^{14} for a complete layer so that the true surface was 1.347 times the apparent surface (Ref 58:325). In similar experiments Bosworth and Rideal (Ref 15:25) studied the condensation of potassium on tungsten ribbons and found the ratio of true to apparent surface to be 3-4 rather than 1.3. This roughness factor tended to decrease with time, however, which seems to indicate that the tungsten ribbon was insufficiently aged.

Equations Describing Adsorption. In order to describe surface adsorption quantitatively, the concentration of atoms in a complete monatomic film is given the symbol ∇_1 . If the actual concentration of adsorbed atoms per cm^2 on the surface is ∇ , then we may define the fraction of the surface covered by adsorbed atoms, θ , as

$$\theta = \frac{\nabla}{\nabla_1} \quad (15)$$

If the molecules of a gas in contact with a solid impinge on the solid at the rate of μ molecules per cm^2 per second and if ν is the rate at which they evaporate from the surface, then the rate at which the surface concentration, \bar{v} , increases is given by

$$\frac{d\bar{v}}{dt} = \alpha\mu - \nu \quad (16)$$

where α is the fraction of molecules striking the surface which condenses. Taylor and Langmuir have demonstrated conclusively that, for cesium striking tungsten, α is equal to unity even when θ is as great as 0.98 (Ref 97).

For the steady state case $\frac{d\bar{v}}{dt}$ is zero and

$$\alpha\mu = \nu \quad (17)$$

If the number of atoms per cm^2 that are evaporated each second is divided by the total number of atoms per cm^2 on the surface, we obtain the fraction of adsorbed atoms evaporated each second. Or, looking at another way, we obtain the probability that any one atom will be evaporated in one second. The reciprocal of this probability gives the mean lifetime, τ , of an adsorbed atom on the surface.

$$\tau = \frac{\bar{v}}{\nu} \quad (18)$$

The rate of evaporation will depend on the nature of the adsorbed atoms and the surface. But we might expect that it would increase with temperature according to the relation

$$v = \text{const.} \exp\left(\frac{-\lambda}{kT}\right) \quad (19)$$

where λ is the work required to remove an adsorbed atom from the surface.

When an atom strikes a surface which is partially covered with adsorbed atoms it may strike other adsorbed atoms and form a second layer. Exactly what happens in this case depends on whether the impinging atoms have a greater affinity for the atoms of the underlying solid or for other adsorbed atoms. The situation is best illustrated by the example of water vapor condensing on a solid surface. If the surface is "wetable," a monomolecular film completely covers the surface. This implies that the water molecules are attracted more strongly to the surface atoms of the solid than to each other. If, on the other hand, the affinity of the water molecules for each other is greater than for the underlying solid, the surface is said to be "non-wetable" and the first few water molecules to condense on the surface act as nuclei for condensation. Instead of a monomolecular film forming, clusters of water molecules form isolated droplets on the surface.

For the cases of interest, namely alkali metals on high work function surfaces, monomolecular films form because atoms in the first layer tend to become ionized and are held to the surface by strong coulomb forces, while atoms in subsequent layers are not necessarily ionized, and hence, are bound less firmly.

If we assume that the forces between neighboring atoms are weak compared to the forces binding the atoms to the solid, we may conclude that the average lifetime, τ , of an adsorbed atom is independent of the number of adsorbed atoms on the surface. Therefore, according to equation (18), the evaporation rate, ν , is proportional to the surface concentration, Γ , and also to the covering fraction, θ . We can write the expression for ν as

$$\nu = \nu' \theta \quad (20)$$

where ν' is the evaporation rate from a completely covered surface and is a function of temperature given by an equation of the same form as (19).

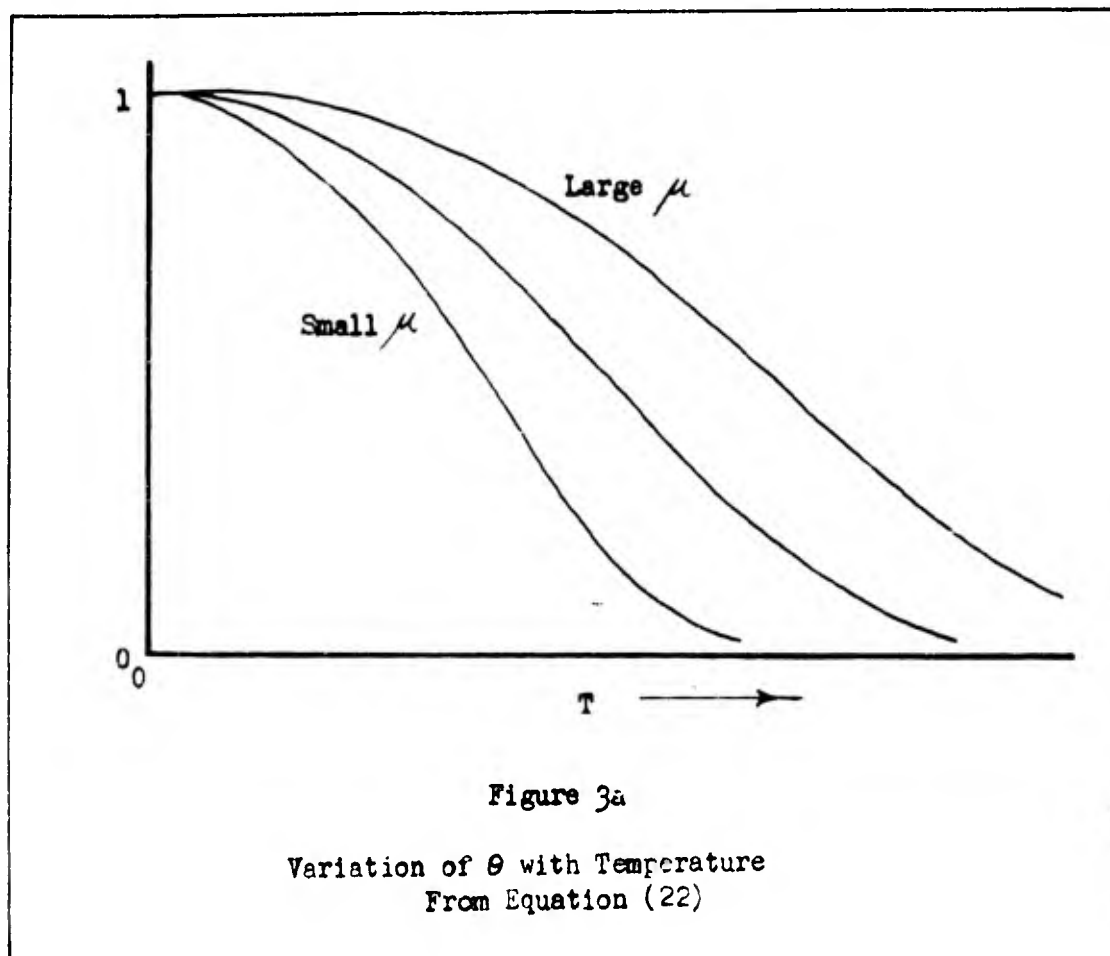
We may assume that a fraction, α_0 , of the incident atoms striking the bare surface of the solid condenses and that those striking atoms in the first layer either do not condense at all or re-evaporate so quickly that a second layer does not form. Since $(1 - \theta)$ is the fraction of the solid surface which is bare of adsorbed atoms, the number of atoms which are deposited per cm^2 per second is

$$\alpha \mu = \alpha_0 (1 - \theta) \mu \quad (21)$$

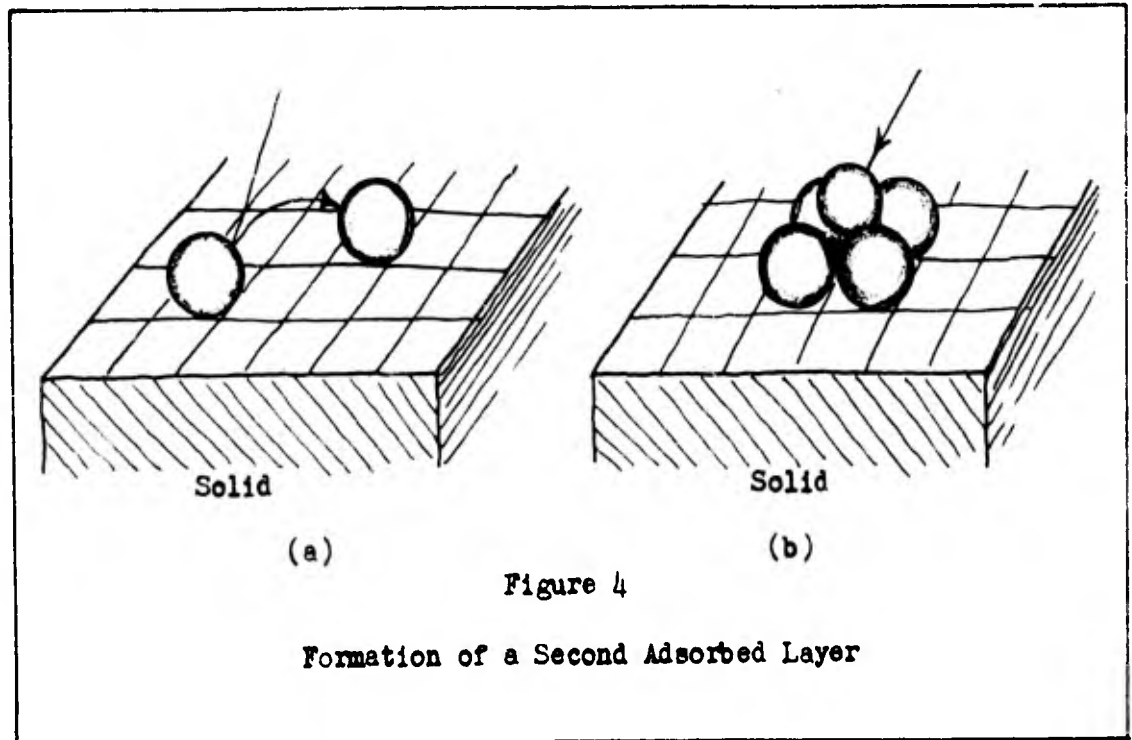
We may now combine equations (17), (19), (20), and (21) to obtain an expression for the equilibrium concentration of adsorbed atoms on the surface:

$$\theta = \frac{\alpha_0 \mu}{\text{const.} \exp\left(\frac{-\lambda}{kT}\right) + \alpha_0 \mu} \quad (22)$$

Figure 3a shows the form of equation (22) and illustrates the fact that the covering fraction depends both on temperature and the rate at which atoms impinge on the surface.



The assumptions leading to equation (22) were very crude, so it should only be considered as approximate. Actually, an incident atom striking an isolated adsorbed atom will slip immediately into the first layer since at least three and usually four atoms must be in adjacent elementary sites in the first layer before an elementary site for adsorption even exists in a second layer. This is illustrated in figure 4.

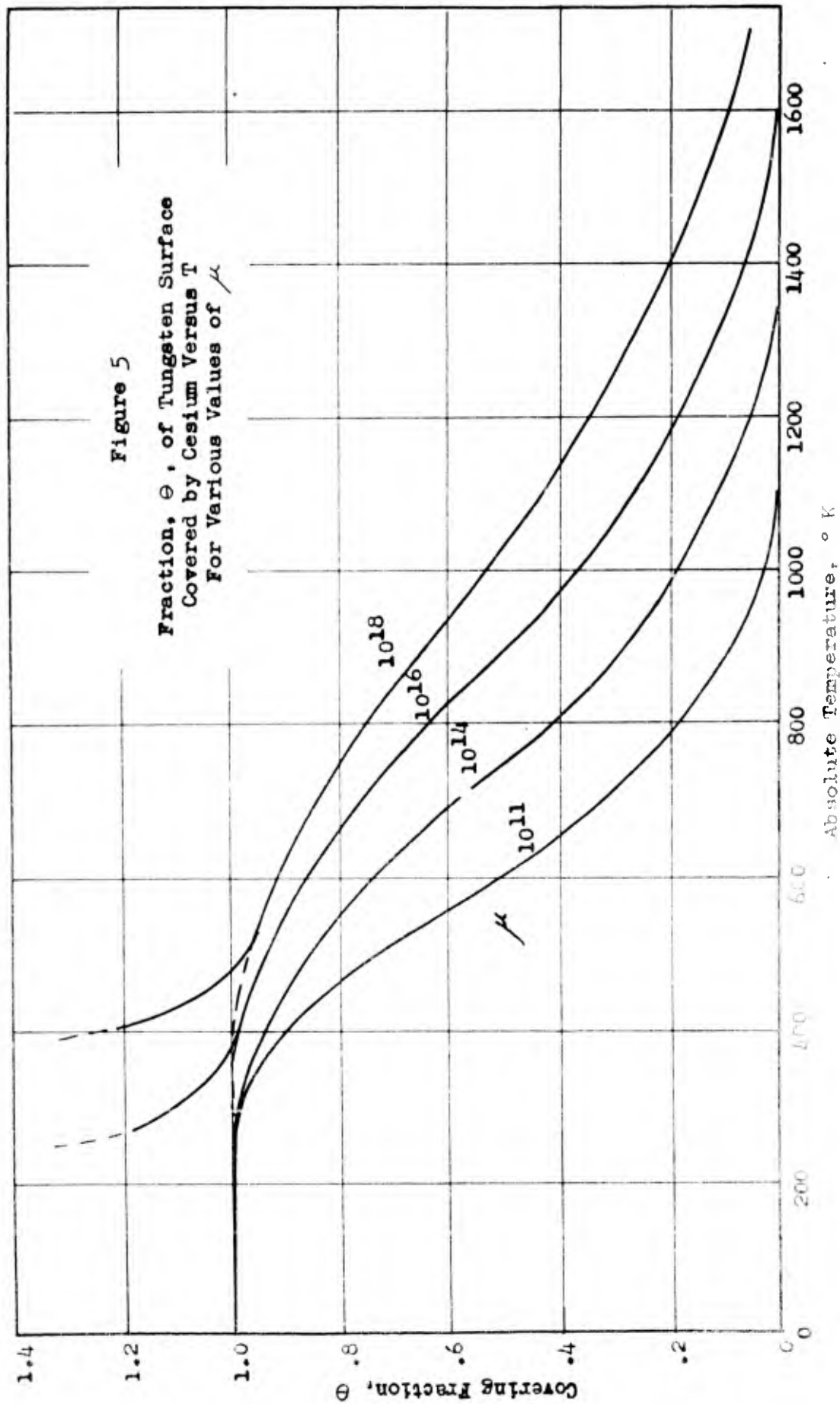


The effective "bare" surface, therefore, is not $(1 - \theta)$ as indicated above, but rather, $(1 - \theta^n)$; where n is a number greater than the number of underlying atoms necessary to create a site for adsorption in the second layer. The reason that n must be greater than 4 in the case illustrated in figure 4(b) is that there is a finite probability that the impinging atom will rebound and find a vacant place in the first layer. Thus, a more reasonable expression for the equilibrium covering fraction, θ , is

$$\left[\text{const.} \exp\left(\frac{-\lambda}{kT}\right) \right] \theta = \alpha_0 (1 - \theta^n) \mu \quad (25)$$

Figure 5 shows experimental values of θ versus temperature for cesium impinging on tungsten. It should be noted that the general shape of the curves is similar to that predicted by equation (22).

504 10/20/20 12.5.2

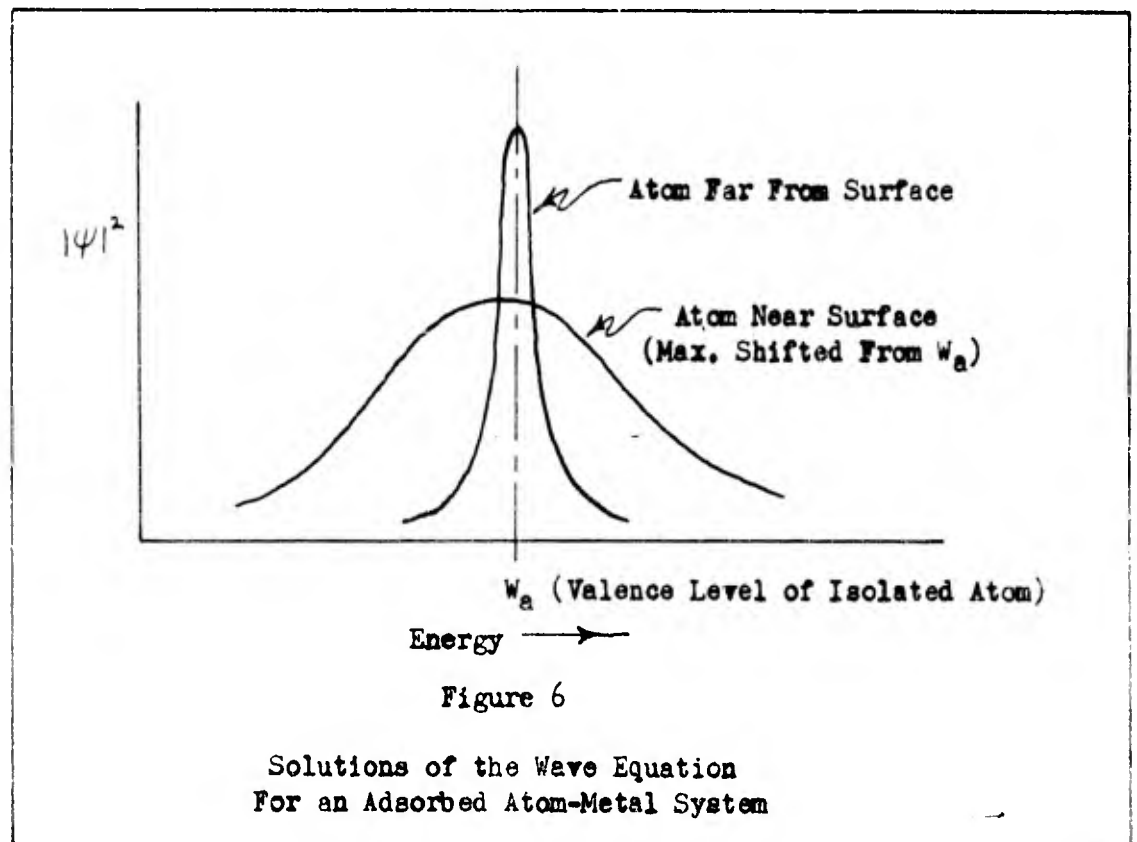


The Formation of an Electrical Double Layer. An electrical surface double layer refers to an unsymmetrical distribution of electrical charge at a phase boundary. The double layer can arise from several sources. The simplest example is the thermionic emission of electrons from a heated metal. The Fermi electron gas is sometimes considered to extend slightly beyond the solid boundary of the metal, somewhat like an atmosphere. This negative space charge, just above the surface, gives rise to an electrical double layer that is negative outward and, hence, retards the escape of electrons. It is this natural electrical double layer and the potential barrier associated with it that accounts for a part of the work function of a clean metal surface.

However, when surface films of foreign atoms are present, the distribution of electrons and positively charged particles on the surface depends on the relative affinity of the positive ions of the underlying metal and the atoms in the adsorbed film for electrons, and, in general, an additional double layer is produced by the surface film. If this has the negative side outward it is called an "electronegative layer" and it increases the work of extraction of electrons; if the positive side is outward it is called an "electropositive layer" and the electron work function is decreased.

It is not necessary for the adsorption of an electropositive layer that the valency electrons of the adsorbed atoms should leave them completely; a tendency to go over to the underlying atoms without passing completely out of the sphere of the surface atoms produces a double layer positive outward.

The energy relationships which determine whether the valency electrons are completely or only partially removed into the underlying metal have been discussed on a quantum-mechanical basis by de Boer (Ref 21) and Gurney (Ref 38). They point out that, when the energy levels of a metal and an adsorbed atom are treated as a single system, the valence electron level is transformed into a quasi-continuous band of allowed energies, the maximum of which is shifted from the discrete valence level of the isolated atom (See figure 6).



The width of the band and amount of shift depend on the distance between the adsorbed atom and the metal. There is a critical spacing at which the intense electron exchange between the adsorbed atom and the metal makes the atomic and ionic states of the atom indistinguishable. The time

averaged charge of the adsorbed atom can thus vary between zero and the electronic charge, depending on the atom-metal spacing.

Table II
Work Function of Tungsten
(Adsorbed Layer 1 or 2 Atoms Thick)

Clean Tungsten	4.54 ev
Tungsten-Oxygen	9.23
Tungsten-Thorium (half-covered)	3.20
Tungsten-Thorium	2.63
Tungsten-Cesium	1.6
Tungsten-Oxygen-Cesium	0.71
Tungsten-Barium	1.56
Tungsten-Oxygen-Barium	1.34

(From Ref 1:313)

Table II illustrates the effect of a complete monatomic film of various adsorbed atoms on the work function of tungsten. Note that an electronegative film such as oxygen between the tungsten and an electropositive layer increases the electropositive nature of the surface film. A complete film of cesium on tungsten lowers the work function 2.94 ev, while a cesium film on top of an oxygen film lowers the work function 3.83 ev. The difference in electron affinity between tungsten and cesium is less than the difference in affinity between oxygen and cesium. In the latter case the cesium is more completely ionized and the positive ions are bound more firmly to the solid.

The change in work function of a metal when an adsorbed film is present is called the contact potential of the film. Figure 7 shows how the contact potential of a cesium film on tungsten varies as a function of the covering fraction, θ . It is a general property of electropositive

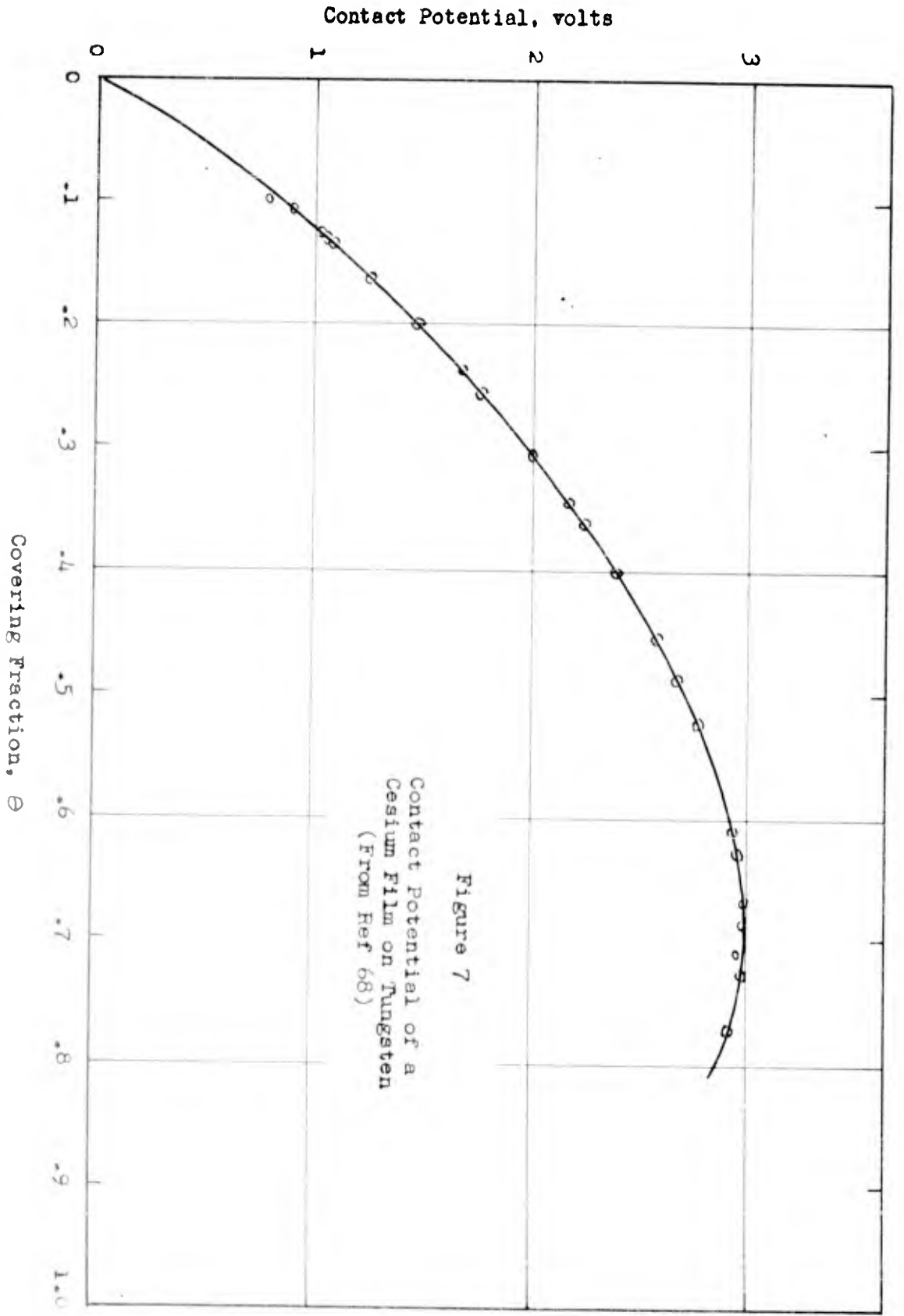
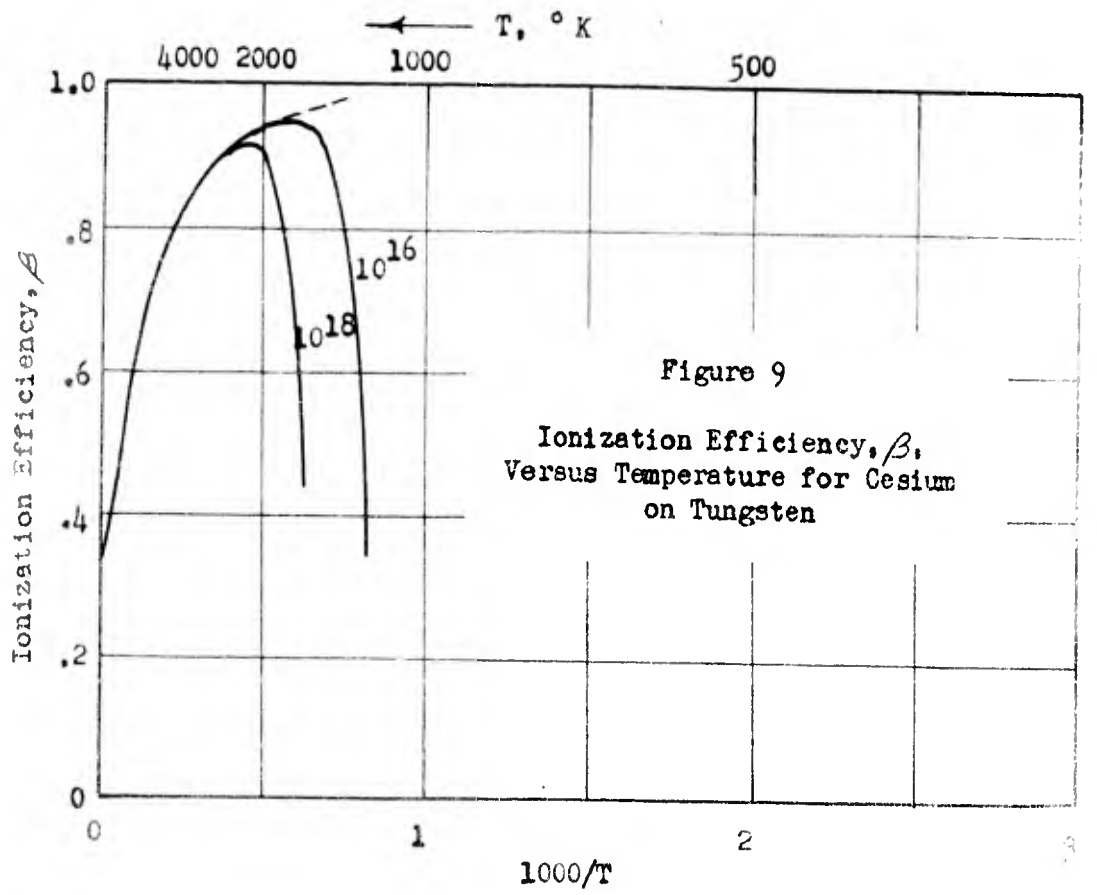
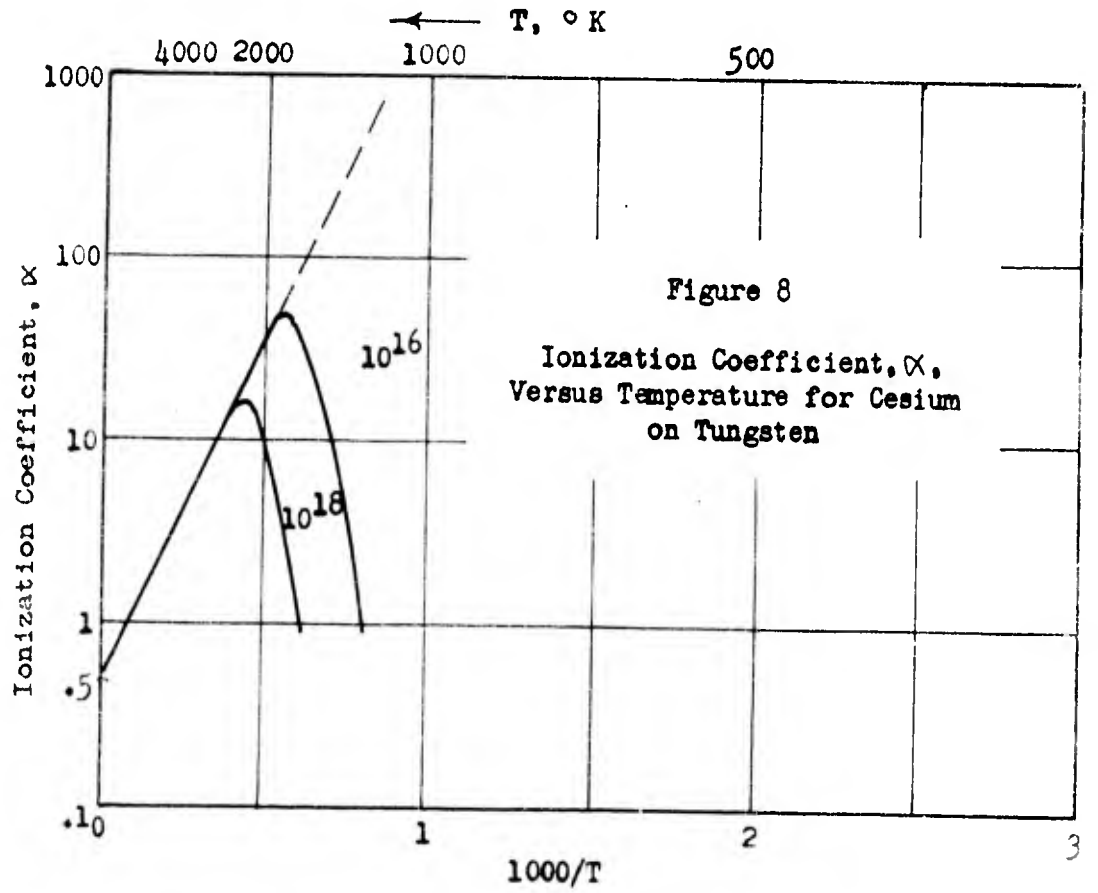


Figure 7
 Contact Potential of a
 Cesium Film on Tungsten
 (From Ref 68)

films on tungsten that the contact potential reaches a maximum when the surface is about 70% covered.

The Critical Temperature for Ionization. From the information contained in figures 5 and 7 we can plot the Saha-Langmuir equation for cesium and tungsten, taking into account the variation of the work function due to the adsorbed film. This is done in figure 8. We note immediately that an optimum temperature exists for maximum surface ionization. If the temperature drops below the optimum value, the adsorbed film grows, causing a decrease in the work function and a corresponding decrease in surface ionization. Langmuir has determined that the maximum surface ionization occurs when Θ is about .01 (Ref 58). The temperature at which this equilibrium concentration exists depends, of course, on the rate at which cesium atoms are impinging on the surface.

In deriving equations (22) and (23) for the equilibrium covering fraction, Θ , we assumed that forces between neighboring atoms were weak. This was equivalent to postulating that the adsorbed film constituted a two-dimensional "perfect gas." Just as in three-dimensional real gases, however, forces between atoms can cause condensation into a dense two-dimensional "liquid phase" in which atoms are closely packed. Langmuir showed that there was a narrow temperature range in which these two phases, "adsorbed gas" and "adsorbed liquid," were in equilibrium with each other. The initial appearance of the denser phase was shown to depend on the growth of nuclei which were presumed to exist at surface irregularities such as dislocations or crystal boundaries. A slight change in temperature,



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either way, could cause the phase boundary to move rapidly until the entire surface was covered with only one phase.

In his experiments with cesium and tungsten, Langmuir noticed that, if the rate of arrival of atoms at the surface was kept constant and the temperature was gradually raised, a discontinuity set in at a fairly definite critical temperature, and the ion current rose rapidly to a very high value, corresponding to nearly 100% ionization. Furthermore, if the temperature was lowered slowly, the ion current dropped discontinuously to a low value; but this occurred at a temperature lower than the previously mentioned critical temperature. Langmuir attributed this sudden change in surface conditions and the hysteresis effect associated with it to the transition between the two stable surface phases. Taylor and Langmuir (Ref 90) expressed the relationship between critical temperature, T_c , and μ by the equation

(Cesium on tungsten)

$$\log_{10} \mu = 27.791 - 14350/T_c$$

where T_c is expressed in degrees Kelvin and μ is in atoms per cm^2 per second.

Killian (Ref 49) found exactly the same phenomena for rubidium and potassium ionized on tungsten. The following equations for T_c were derived from the data of Killian:

(Rubidium on tungsten)

$$\log_{10} \mu = 27.95 - 15700/T_c$$

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⊙
(Potassium on tungsten)

$$\log_{10} \mu = 25.17 - 11300/T_c \quad (26)$$

Contrary to what many authors imply, the critical temperature is not necessarily the point of maximum ionization efficiency, but merely the temperature below which ionization is very inefficient. Figure 8, for example, shows that, for a μ of 10^{16} atoms per cm^2 per second, the optimum temperature for ionization is about 1700°K , while the critical temperature computed from equation (24) is only 1220°K .

Effects of an Electric Field

Schottky Effect. Just as an electric field, tending to pull electrons from the surface, can lower the effective work function of a metal, so also can a field, tending to oppose electron emission, raise the effective work function. This is known as the "Schottky effect." Zandberg and Ionov (Ref 104) have shown that for weak fields (less than 10^6 volts per cm) the work function, ϕ , in the Saha-Langmuir equation should be replaced by the effective work function ϕ' , where

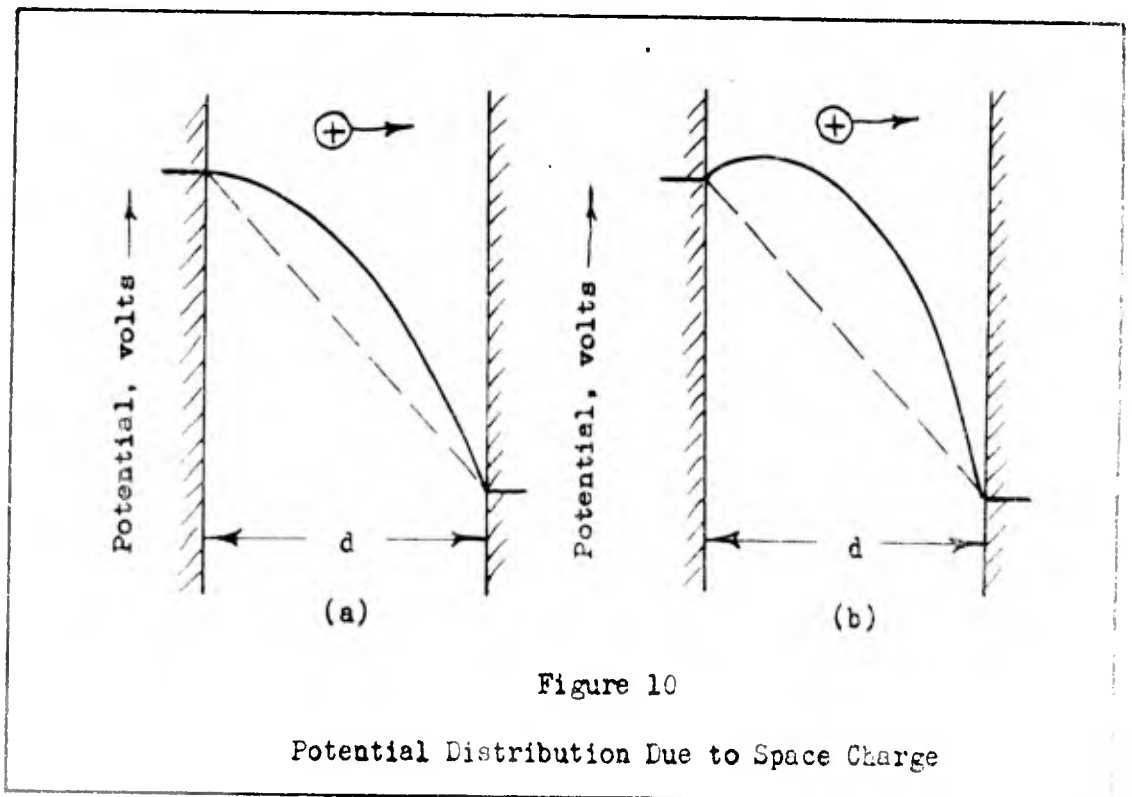
$$\phi' = \phi + (eE)^{1/2} \quad (27)$$

Space Charge Limitation. If no convection current flows between two parallel electrodes a distance, d , apart that are at different potentials, the electric field between them is given by

$$E = V/d \quad (28)$$

where V is the difference in potential

If charged particles are allowed to flow between the electrodes, the charges in transit will set up a field opposing the initial field. The net result will be that the field (voltage gradient) at the emitting electrode will drop to zero and the field at the collector will be $4/3$ of its non-flow value. This is illustrated by the voltage curves of Figure 10(a)



Once this condition is reached, the flow is said to be "space charge limited," and no increase in the number of particles available at the emitter surface will result in more reaching the collector. If, in fact, more particles are emitted than can be carried to the collector, the potential curve of Figure 10(b) results, and the field at the emitter surface turns back the excess particles. So long as the supply of charged particles at the emitter is unlimited, the current increases with the

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$3/2$ power of electrode voltage. This is the well known Child's law relationship. If the supply of charged particles is limited, then increasing the electrode voltage beyond the saturation point results in very little increase in current. Beyond this point the current is "emission or source limited." The slight increase in current with voltage beyond the saturation point is due to the Schottky effect.

III. A Discussion of Experiments on Surface Ionization

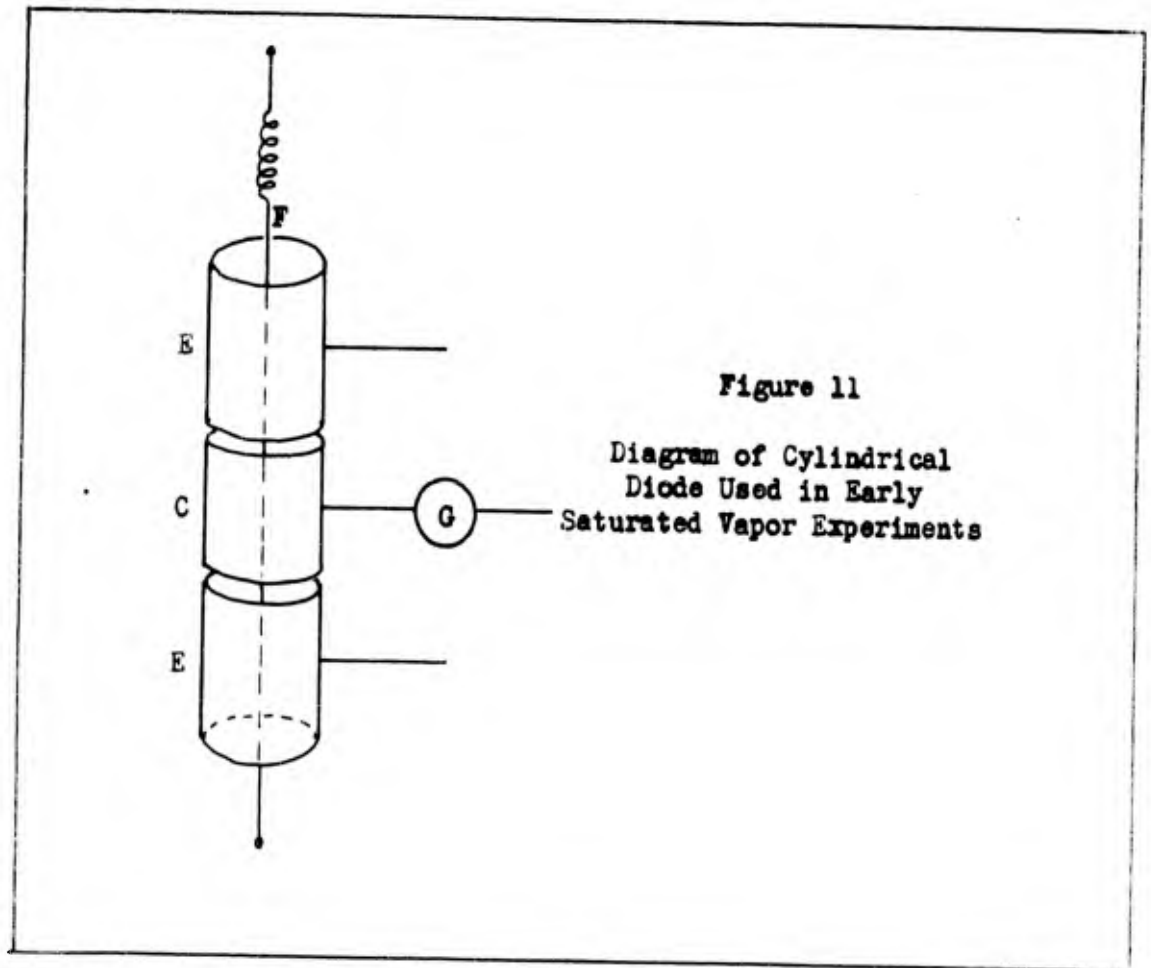
In the preceding chapter we have outlined the theory of surface ionization. The purpose of this chapter is to discuss pertinent experiments in an effort to determine how well the theory is supported by experimental results.

Experimental Techniques

In all experiments on surface ionization, molecules of some element are allowed to contact a heated metal surface. An electrode, negative with respect to the heated metal, is placed nearby and the current from the heated filament is measured as a function of the filament temperature, electrode voltage, and the rate at which molecules impinge upon the filament.

At present there are three basic methods for investigating surface ionization, differing mainly in the method of supplying molecules to the surface of the heated metal.

Saturated Vapor Technique. The earliest method, used by Langmuir, is called the "saturated vapor" or "bulb" technique. The apparatus consists of a cylindrical diode (see Fig. 11) in which the axial tungsten filament (F) acts as the ionizing surface. The concentric cylindrical electrode is divided into three sections; the center section (C) collects the ion current from the filament, and the two end sections (E) act as guard rings to minimize end effects.



Alkali metal vapor is distilled into the evacuated glass bulb containing the diode, and the whole apparatus is sealed. The bulb is then immersed in a liquid bath at a carefully controlled temperature.

The rate of arrival of alkali metal atoms at the surface of the filament may be calculated according to the laws of the kinetic theory of gases as

$$\mu = \frac{P}{(2\pi m kT)^{1/2}} \quad (29)$$

where μ is the rate of arrival in atoms per cm^2 per second and m is the mass of the atom. If the relationship between the vapor pressure, p , and temperature, T , is known, μ can be calculated. Unfortunately, the vapor pressure of alkali metals is not accurately known and this leads to a major source of error in the saturated vapor experiments.

The collector ring (C) and the end rings (E) are kept at some voltage negative with respect to the filament (F). The positive ions formed at the filament are drawn radially outward by the electric field and those striking the collector ring are measured as a current by a suitable galvanometer instrument (G).

Since the filament is generally quite hot, photons from the incandescent filament strike the inner surface of the collector rings and release photo-electrons which add to the current measured by G. In addition, positive ions, striking the collector rings at high velocity, knock secondary electrons out of the surface which combine with the photo-electrons to give erroneously high current readings. Because the photo current rises rapidly with the filament temperature, and secondary electron current depends on filament-collector voltage, some means of suppressing the flow of electrons from the collector to the filament is necessary if large errors are to be avoided. Early experimentors limited filament temperatures to below 1700°K where photo currents could be neglected. Most modern experiments utilize highly transparent suppressor grids or axial magnetic fields to deflect secondary electrons.

Langmuir had available accurate tables (Ref 47) from which he could determine the temperature of the tungsten filament as a function of the

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filament diameter and heating current. However, since the temperature of the whole apparatus was varied through a wide range in order to obtain different values of μ , radiation corrections had to be applied. In addition, corrections for heat losses by conduction from the ends of the filament were necessary (Ref 63). It should be noted that most tables, such as were used by Langmuir, are only applicable to tungsten of extreme purity which has been subjected to a prescribed heating and aging process. Zandberg (Ref 101) points out that for commercial grade tungsten, such as he used, optical micropyrometer values and table values differed by as much as 200°C.

Langmuir assumed that the rate at which alkali atoms impinged on the filament was independent of the temperature of the filament. It is reasonable to expect, however, that the temperature of the collector surfaces is not the same as that of the bath in which the whole apparatus is immersed. Since the rate of evaporation of alkali atoms from the collector surfaces affects μ , some error results from assuming that the characteristic temperature of the alkali vapor is equal to the bath temperature.

Molecular Beam Technique. In order to eliminate errors due to photoelectric currents and allow measurements of ionization efficiencies to be made at temperatures as high as 2800°K, Copley and Phipps (Ref 19) introduced the molecular beam technique. Figure 12 shows a diagrammatic sketch of their apparatus. In this method the atoms of alkali metal vaporize through a small hole (A) in a specially constructed oven. The molecular beam is defined by a narrow slit (D) and allowed to pass through slice (E) in the collector ring (C) and strike the filament (F). The molecular

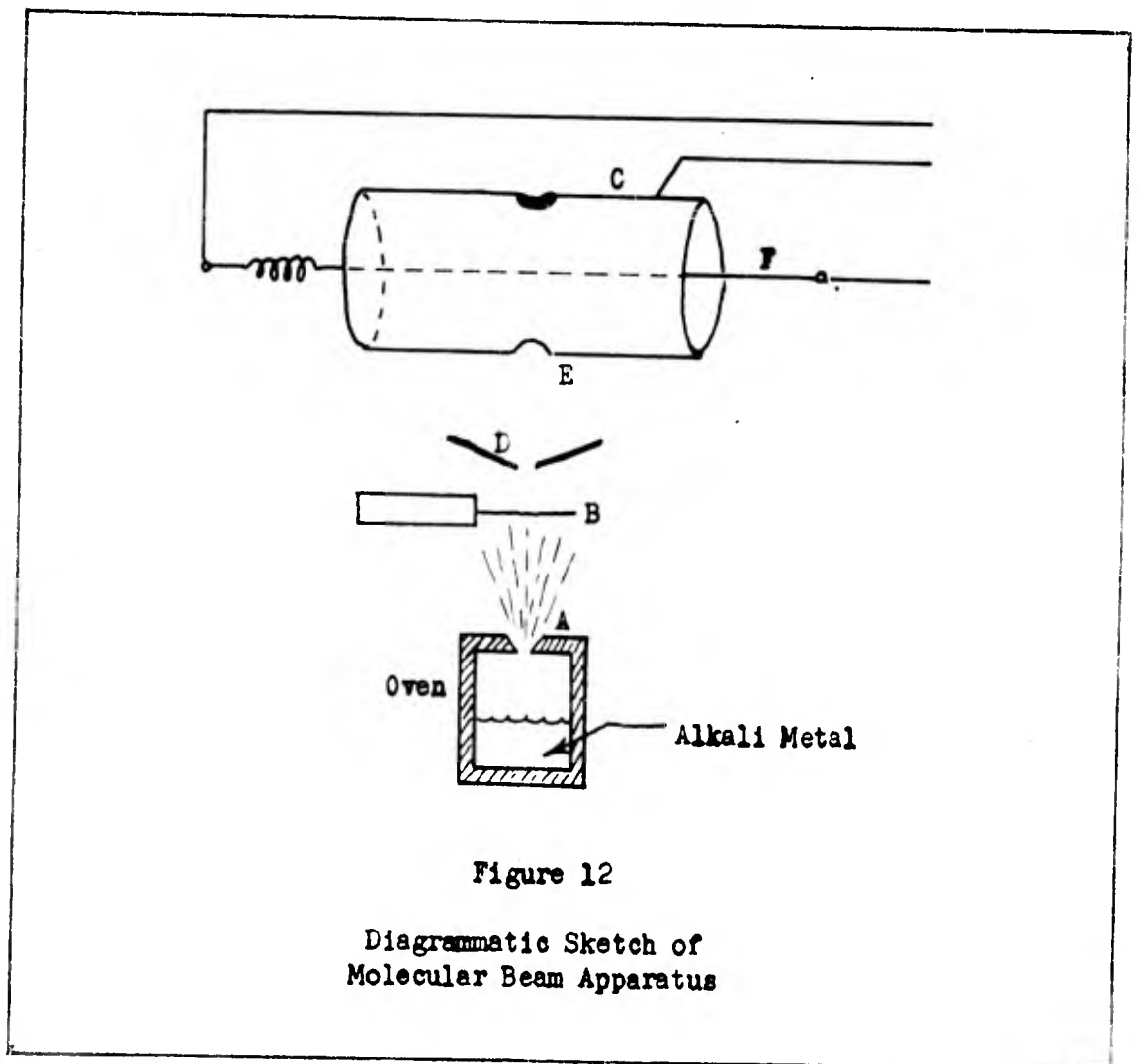


Figure 12

Diagrammatic Sketch of
Molecular Beam Apparatus

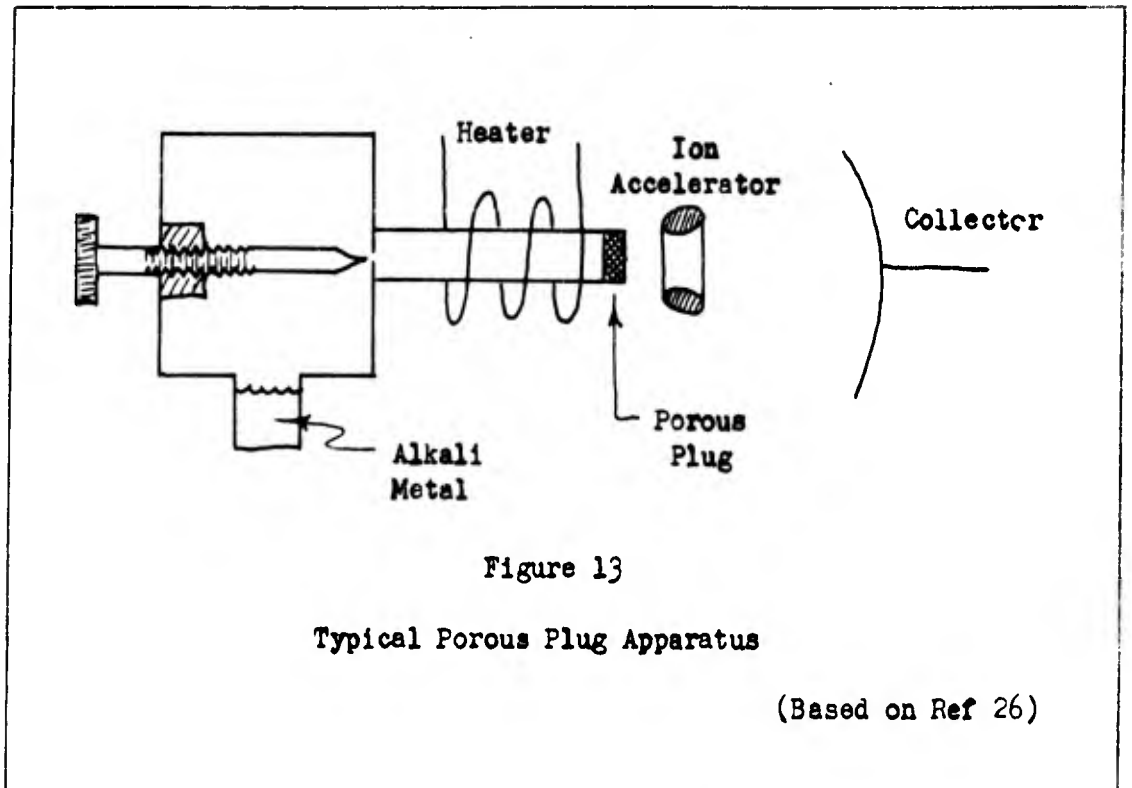
beam is accurately centered on the filament by visually aligning the filament with slot (D) and hole (A). A magnetically operated shutter (B) can interrupt the beam, shutting off the flow of alkali atoms to the filament.

The current which is measured when the shutter is closed is assumed to be due to the photo electric effect. If the apparatus is not thoroughly aged and outgassed, however, some of this stray current can be due to trace alkali impurities in the filament metal as well as characteristic ions of the filament metal which evaporate at high temperatures. Impurity alkali

ions have been observed issuing from heated molybdenum filaments as much as eleven hundred hours after they were first heated (Ref 37, 45, 48, 22, 7, 86). At any rate, the stray current is not due to ionization of impinging alkali atoms. The molecular beam technique, therefore, allows this source of error to be eliminated. The difference in the current with the shutter open and closed is still not the true surface ionization current, since secondary emission of electrons may still be present.

Morgulis (Ref 70) was the first to use an axial magnetic field to deflect secondary electrons, and Zandberg (Ref 102) introduced a 98% transparent suppressor grid which proved more effective than the magnetic field. In addition to eliminating photo electron errors, the molecular beam technique reduces the influence of filament temperature on the rate of arrival of atoms at the surface of the filament.

Porous Plug Technique. The third and most recent method for investigating surface ionization is the porous plug technique. A typical porous plug device is illustrated in Figure 13. Alkali metal vapor is allowed to diffuse from a special oven through a porous plug of sintered tungsten or other refractory metal which is heated indirectly by radiation from an adjacent filament. As the alkali metal diffuses out the pores and over the surface of the plug, an electric field draws the positive ions from the surface to a collector. Just as in the molecular beam method, the feed of alkali atoms to the heated surface can be shut off, allowing photo electric effects to be measured. Suppressor grids can also be used to discourage secondary emission.



The big disadvantage to this method as a basic research tool is the lack of information on the diffusion of alkali atoms through porous metals and the absence of any reliable method of measuring the rate of arrival of atoms at the surface. As we will see in a later section, however, the porous plug method is the most attractive means of supplying positive ions for an ion propulsion rocket engine, and so, most future work will probably involve this technique.

Results of Experiments

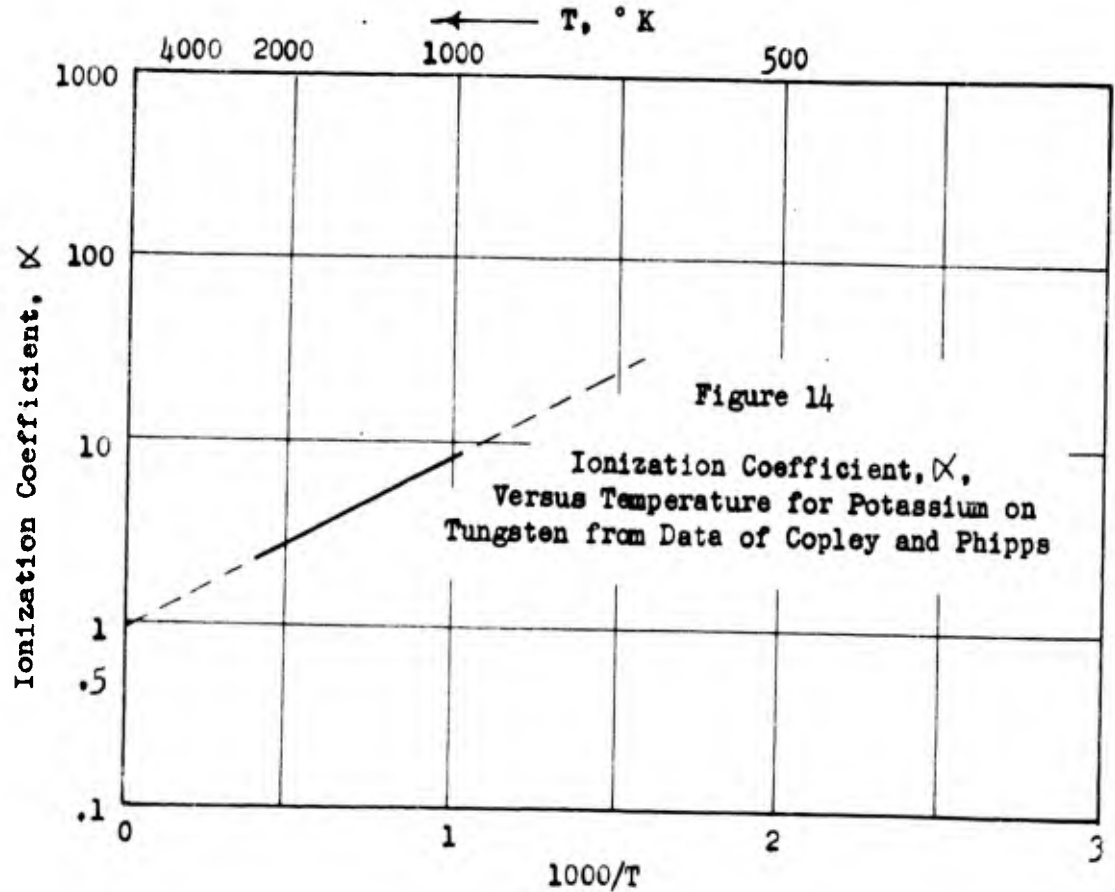
Since 1923, experimentors have investigated the ionization of all the alkali metals and many alkali halides on pure tungsten ionizers. In addition, some alkali metals and alkali halides have been ionized on platinum (Ref 20), molybdenum (Ref 29), rhenium (Ref 4), and carbon (Ref 8). In

every case, the theory of surface ionization, as described in Chapter II, has been verified qualitatively. Quantitatively, however, many experiments showed large discrepancies from the values predicted by equation (10).

Alkali Metals on Tungsten. One of the earliest quantitative checks on the Saha-Langmuir equation was the work of Copley and Phipps (Ref 19) in which they used the molecular beam technique to measure the ionization of potassium on tungsten. In order to measure the rate of arrival of potassium atoms at the ionizing filament, they allowed the filament to become oxidized by heating to 1640°K in the presence of air, and then measured the ion current from the oxidized filament, assuming 100% ionization from the high-work-function surface (See Table II). After each measurement the filament was cleaned of adsorbed oxygen by flashing to a high temperature.

The data of Copley and Phipps is represented by the solid line in Figure 14. From the slope of the line they measured an effective work function of 4.52 volts for tungsten. The intercept with the vertical axis indicated a constant coefficient of 1 rather than $\frac{1}{2}$ in equation (10). They attempted to explain this discrepancy by suggesting that the work function varied with temperature. Later experiments showed that different temperature coefficients were calculated from the ionization of different elements on tungsten in the same temperature range, thereby invalidating their explanation.

It remained for Zemel (Ref 106) in 1958 to derive a modified Saha-Langmuir equation for patchy surfaces which would account for the data of Copley and Phipps and others. This equation has already been derived as



equation (14) in Chapter II. Zemel used a four-patch model illustrated by Table III to account for the potassium-tungsten data.

Table III
Patch Work Functions and Fractional
Areas Used by Zemel Compared with
Values of Herring and Nichols*

ϕ_k	f_k	
	Zemel	Herring/Nichols
4.35	0.12	0.089
4.56	0.23	0.254
4.68	0.47	0.343
5.35	0.18	0.271

*From Ref 41:223

The values of f_k are compared to those measured by Herring and Nichols (Ref 41:223) from thermionic emission studies. The agreement is fairly good; but, since equation (14) contains an arbitrary number of adjustable parameters, one can argue that Zemel's selection of four ϕ_k 's and f_k 's is not unique. The important fact that Zemel's theory illustrates is that the Saha-Langmuir equation, in the form of equation (10), cannot be used to describe surface ionization on polycrystalline surfaces.

A simple equation such as (10) can be used over a limited temperature range by selecting an "effective work function" for the patchy surface. It should be noted, however, that the effective work function, as determined from thermionic emission data, is generally too low. This is because the patches of low work function, though occupying only a small fraction of the surface, contribute most of the thermionic current; while in surface ionization, the patches of high work function predominate.

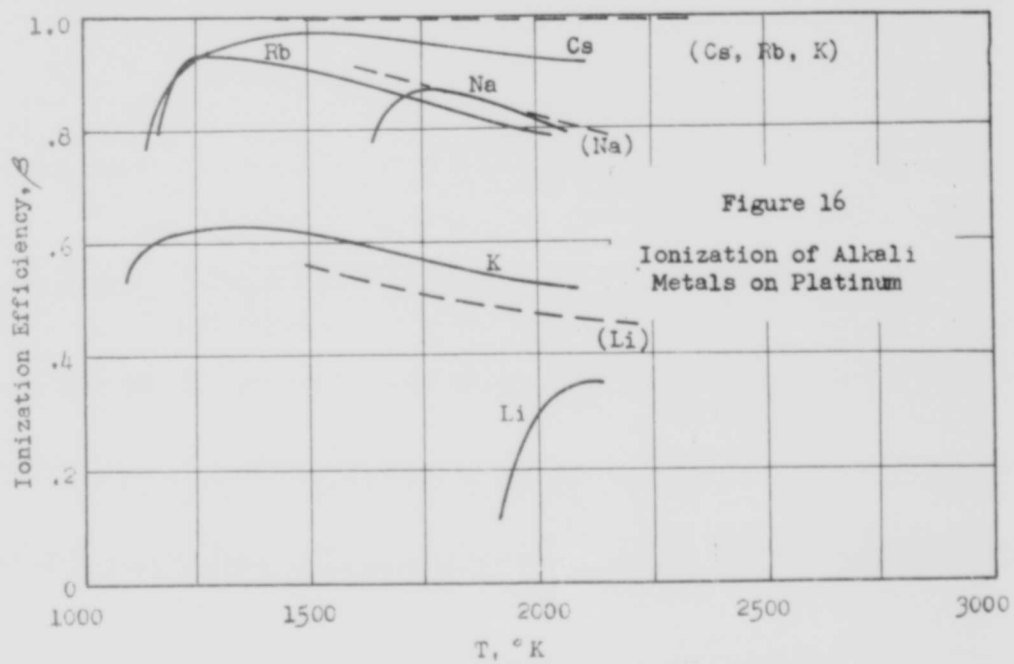
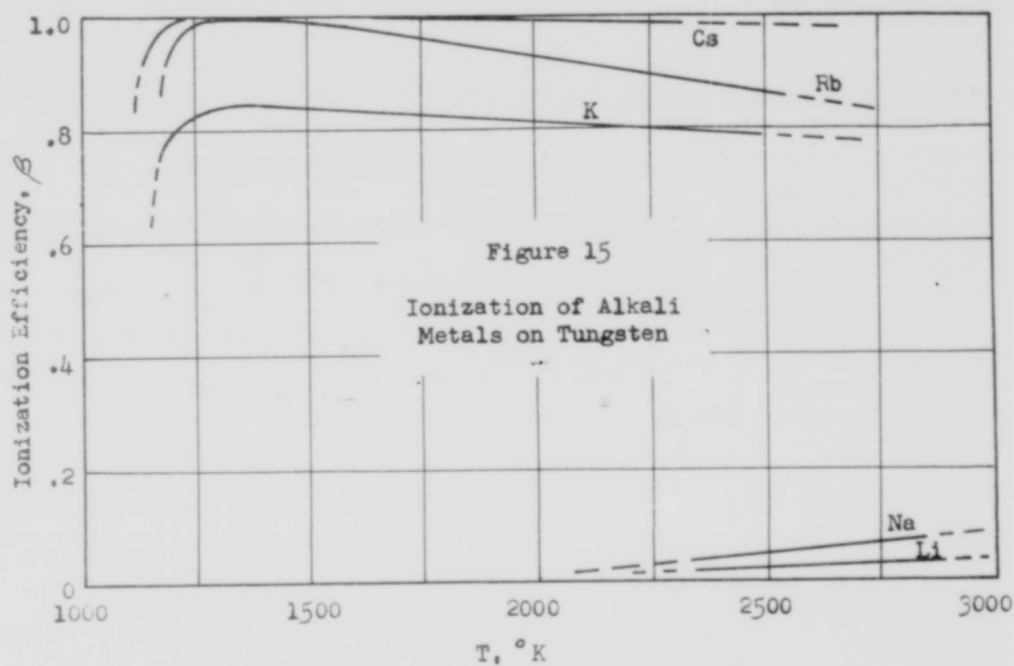
Alkali Halides on Tungsten. The surface ionization of alkali halides on tungsten has been investigated by Phipps and his coworkers (Ref 19, 46, 40) and by others. All observers found that, when alkali salts such as potassium iodide or potassium bromide were ionized on hot tungsten, the results were almost identical, within experimental errors, to those obtained with the pure alkali metal. This fact suggests that the alkali halide molecules become completely dissociated on the surface and the halogen atoms evaporate as neutrals. There is evidence (Ref 40) that at lower temperatures halogen films are adsorbed on the tungsten. Such films would be electro-negative and raise the work function. However, alkali ions, adsorbed on top of the halogen film, would form a strong electro-positive

layer; and so the net effect is about the same as if the alkali ions were adsorbed directly on the tungsten.

Alkali Metals and Halides on Platinum. If there is any experiment that sheds real doubt on the validity of the Saha-Langmuir equation it is the work of Datz and Taylor (Ref 20) with platinum. The effective work function of polycrystalline platinum, as determined from thermionic emission data, is 5.32 volts (Ref 42), the highest of any known metal. We would expect, therefore, that the ionization efficiency on platinum would be very high. Figures 15 and 16 show the results obtained for cesium, rubidium, potassium, sodium, and lithium on pure tungsten and pure platinum, respectively. The values of ionization efficiency for tungsten in Figure 15 agree with theory. In Figure 16, however, only the curve for sodium agrees with the theoretical values for ionization on platinum (plotted as dashed lines on the graph).

Datz and Taylor explain the low ionization efficiencies on platinum by postulating a high reflection coefficient for incident atoms. They associate this high reflection coefficient with a low probability for electron exchange between the adsorbed atom and the platinum surface.

In the investigation of the reverse process (neutralization of an ion at a hot metal surface) it has been found that a high probability for electron exchange exists when an electron in the conduction band of the metal corresponds exactly in energy to the valence level of the adsorbed ion. On this basis, Datz and Taylor concluded that ionization of an adsorbed atom would be most probable if there existed vacancies in the band structure of the metal corresponding in energy to the electron in the



ground state of the adsorbed atom. They reasoned that platinum may have few such vacancies in its band structure, whereas tungsten should have many, owing to the configuration of the outer electrons.

The ionization of alkali halides on platinum is altogether different from what occurs on tungsten. Whereas on tungsten, the halides behaved almost like the pure alkali metal, on platinum even the different salts of potassium behaved differently. For all the halides on platinum, ionization efficiency was extremely low (0.25 for KF, less than 0.01 for KI, KCl, and KBr). Datz and Taylor were completely at a loss to explain this discrepancy. A large reflection coefficient, strongly dependent on specific chemical factors, seems to be required to explain the results.

Surface Ionization on Semi-conductors. The results of Datz and Taylor suggest that surface ionization can never be fully understood without a good knowledge of the electronic band structure of the metal surface. Since the energy scheme of semi-conductors is fairly well known, it would seem that the ionization of atoms on semi-conductor surfaces would yield useful information. Morgulis (Ref 71) has treated this subject qualitatively. He maintained that, when the valence level of the adsorbed atom lay within an allowed semi-conductor band, the result would be similar to that for metals; and, when the valence level fell in a forbidden or filled semi-conductor band, electron exchange would be inhibited. The surface ionization on semi-conductors with known energy levels has not yet been investigated experimentally, and so Morgulis' theory has not been tested.

Because of the relatively low melting point of most semi-conductors, however, strong electric fields would have to be used to lower the threshold

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temperature for ionization. In these strong collecting fields, energy level shifts within the semi-conductor would be of major importance.

IV. Application to Ion Propulsion

A practical ion rocket engine requires a copious supply of efficiently produced ions. Surface ionization provides the simplest and the most efficient source of ions for propulsion purposes. The application of surface ionization theory to the design of a practical ion engine is discussed in this chapter.

Choice of Fuel and Ionizer

In choosing a fuel and ionizer combination, several criteria immediately suggest themselves to the designer. The fuel should have a low ionization potential for obvious reasons. Less obvious, perhaps, is the requirement that the "ion propulsion working fluid" have a high mass-to-charge ratio (Ref 65). Since surface ionization is not likely to produce any but singly ionized particles, this requirement means that the fuel should have a relatively high molecular weight. In addition, it should be non-corrosive, easily handled, plentiful, and cheap. It is doubtful if all of these criteria could be met by a single fuel.

The ionizer (sometimes called the emitter) should have a high electron work function and a relatively high melting point. It is also desirable that the ionizer be easily fabricated and compatible with the fuel, i.e., not subject to inter-granular attack.

Tables IV and V list physical properties of some possible fuel and ionizer materials. One should be cautious about accepting the values of work function listed in Table V, however, since the values obtained

experimentally show large variations and always depend on the method used to measure the work function (photo-electric, contact potential, or thermionic emission).

Table IV
Physical Properties of Some Possible Fuels

Element	Ionization Potential, ev	Atomic Weight	Specific Gravity
Cesium	3.87	132.9	1.87
Rubidium	4.16	85.5	1.53
Potassium	4.32	39.1	0.85
Sodium	5.12	23.0	0.97
Lithium	5.36	6.9	0.53

(From Ref 42)

In spite of the fact that cesium and platinum appear to be the best choice, experimental results have shown this combination to be inferior to cesium and tungsten (See Fig. 16). Since more experimental data are available for cesium and tungsten than for any other combination, this has been the almost universal choice of ion rocket designers. No really systematic approach to testing the other promising combinations has been undertaken to date. Besides the pure elements listed in Table V, an almost infinite variety of alloys and cermets would seem to warrant experimental investigation.

While the choice of tungsten as the ionizer material may be premature, cesium, because of its very low ionization potential and high molecular

Table V
Physical Properties of Some Possible Ionizers

Element	Work Function, ev	Melting Point, C
Platinum	5.32	1774
Iridium	5.3	2454
Rhenium	5.1	3167
Nickel	5.03	1455
Palladium	4.99	1549
Rhodium	4.80	1966
Carbon	4.60	3550
Chromium	4.60	1890
Tungsten	4.52	3370
Iron	4.48	1535
Molybdenum	4.20	2620
Tantalum	4.19	2996

(From Ref 42)

weight, appears to be the logical choice for the fuel. Petrick (Ref 77) has conducted corrosion tests with cesium and reports that it is compatible with tungsten, molybdenum, and platinum. In addition, Petrick has investigated the feasibility of reducing cesium metal from its salts, in situ, in order to reduce the handling and storage problem.

Unfortunately, cesium is scarce, and projected costs fall between \$40 and \$200 per kilogram in large quantities (Ref 17:198).

Methods of Feeding Fuel to the Ionizer

The design of an ion source for propulsion can be characterized by the method used to supply fuel to the hot ionizer surface. There are two main classifications; front spray feed systems and porous ionizers or rear replenishment systems.

Front Spray Feed Systems. The spray system is essentially an extension of early experimental techniques, especially the molecular beam method. It consists of allowing a collimated beam of fuel molecules to escape from an oven aperture and strike a hot ionizer surface. This method has several disadvantages. First, it is difficult to collimate the beam so that it strikes only the ionizer. Second, the presence of slow-moving neutral atoms in the ion acceleration region will result in charge-exchange collisions. The slow-moving ions which are formed by such collisions will be pulled into the accelerating electrodes. Since long lifetime is a requirement of ion propulsion systems, the sputtering away of electrode material by the interception of only a small fraction of the ion beam current could be a limiting factor in the engine design.

In an experiment to determine how serious a problem ion interception was, Dulgeroff and his coworkers (Ref 26) measured a sputtering ratio of 10 nickel electrode atoms per incident 10 KV cesium ion. Naiditch, et. al (Ref 74) estimate that all charge exchange collisions occurring from the emitter to the leading edge of the accelerating structure have a 10% probability of producing sputtering damage, and all collisions from there to the output of the decelerator have an 80% probability.

Front spray feeding is not the only way in which neutral fuel atoms can find their way into the accelerating region. If ionization efficiency is less than 100%, a certain fraction of fuel atoms will be emitted from the surface as neutrals. Naiditch calculated that the maximum allowable neutral fraction for a cesium-tungsten source, operating at 1400°K for 300 days with tantalum electrodes, was less than .002 !

Porous Ionizers. In the face of such pessimistic analyses, one is forced to examine the porous plug emitter as the only feasible system for practical, long-life engines. A typical porous ionizer consists of a thin wafer of sintered tungsten powder of approximately 80% theoretical density. Pore size and spacing is irregular in such a material, but typical samples have pore openings of 2-3 microns in diameter and spacings of about 7 microns (Ref 107).

The analysis of ion emission from porous materials is quite complicated. A simplified model of a porous emitter is described in Ref 75, 76, and 107. In these papers, the emitter is assumed to consist of a series of parallel, evenly spaced, cylindrical holes in an otherwise solid plate. The transport of fuel atoms through the holes consists of molecular (Knudsen regime) flow due to a pressure gradient and surface diffusion along the walls of the pore due to a surface concentration gradient. No ionization is assumed to occur within the pores. At the pore exit, those atoms in the gaseous phase continue out the opening and escape as neutral atoms. The surface diffusion component spreads out over the surface of the ionizer and, when the concentration drops to a low enough value, evaporates as ions.

The authors of these papers tried to predict the optimum pore size and spacing as a function of operating temperature and current density, considering cesium as the fuel and tungsten as the ionizer. Their answers are invalid, however, since they are based on values of the surface diffusion coefficient (for cesium on tungsten) obtained by extrapolating Langmuir's data (Ref 62) to higher temperatures. Shelton, in a recent study (Ref 85), has shown that surface diffusion coefficients are actually higher than anticipated from Langmuir's work.

There are, however, certain general conclusions which can be drawn concerning ionization on porous surfaces. These are:

1. The pores should be of micron size or smaller to reduce to a minimum those atoms escaping as neutrals in the gaseous phase.
2. The spacing between pores should be of the order of magnitude of a diffusion length. Otherwise, there are areas which remain bare of adsorbed atoms and are ineffective for producing ionization.
3. The ionizer should not be operated in the space charge limited region, but should be source limited. The voltage should be sufficiently high to remove all of the ions as quickly as they are formed, since the neutral fraction will evaporate regardless of the voltage. Put another way, the porous plug emitter should not be overfed because the atoms, in excess of what the voltage can carry away as ions, will escape as neutrals.
4. The porous ionizer should be operated just above the critical temperature for ionization. Higher temperatures would result

in a shortening of the mean lifetime of an adsorbed atom on the surface and, hence, decrease the diffusion length.

In regard to the last statement above, the critical temperature relationships derived in equations (24), (25), and (26) are based on a uniform distribution of adsorbed atoms. Since this is not the case when the surface is being replenished by diffusion from pores, the concept of critical temperature loses much of its meaning. On a porous ionizer, the region nearest the pore exits may have such a heavy concentration of adsorbed atoms that practically no ionization occurs, while further from the exit, the surface may be in the ion emitting state. The whole surface would not be expected to change suddenly from an atom-emitting to an ion-emitting state as the temperature is raised and, hence, the temperature range in which ion current rises rapidly with increased temperature should be broadened considerably. No experimental data on porous ionizers have been published yet to confirm or deny this effect.

There are also disadvantages to the porous plug which is made from sintered metal powder. The plugs are extremely brittle and subject to cracking from thermal stresses. Attaching the porous plug to the end of a feed tube so that there will be no leakage around the plug is an engineering problem which has received much study (Ref 77). Clamping between gasket material only aggravates the cracking problem. Brazing techniques which use platinum as the braze material have been encouraging, but diffusion of the platinum along the grain boundaries and into the pores after prolonged periods at operating temperatures has been noted. In view of the deleterious effect of contaminating the porous plug with the braze material,

techniques to sinter a plug directly to the end of a tube of the same material are now under investigation.

Another problem which has not been studied is the effect of continuous sintering of the porous plug at operating temperatures. Sintering occurs easily with finely divided metals far below their melting point and may result in the gradual agglomeration of the smaller grains and reduction of the exposed surface area through the action of the surface tension of the solid (Ref 1:238).

Hybrid Configurations. In an effort to eliminate some of the engineering problems associated with sintered plugs, some designers have proposed hybrid configurations, combining the features of the spray system and the porous emitter. These include louvered or perforated plates, staggered ribbons, woven wire screens, and bundles of wires with the fuel flowing axially along the bundle.

Some of these are now under investigation (Ref 77). Only the result of experiments on staggered tungsten ribbons has been published (Ref 74). The staggered ribbons were found to be very inefficient; only 7% of the exposed surface was effective in producing ionization.

Energy Efficiency of the Ion Source.

The ion source energy efficiency has been defined in Ref 80 as

$$\eta_s = \frac{P_b}{P_b + P_r}$$

(30)

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where P_b is the ion beam power (beam current x net acceleration voltage) and P_r is the power radiated from the hot emitter. The power required to vaporize and ionize the fuel is negligible. There are other losses in the engine, such as the acceleration losses due to interception of a part of the beam current by the accelerating electrodes, but these are not associated directly with the ion source and should be considered separately. Kuskevics (Ref 50) considers all losses except these two (radiation and acceleration) as insignificant.

From equation (24) we may conclude that the beam current (and hence, beam power) increases exponentially with $1/T$. The radiation from the emitter increases as T^4 , so beam power increases more rapidly with temperatures than radiation losses and high ion source efficiencies should result from high emitter current densities. In practice, however, current densities may be limited by the maximum tolerable beam interception current at the accelerating electrodes.

Research Problems.

The major difficulty in investigating ionization on porous plugs is the lack of a good method for measuring the ionization efficiency. If there were an accurate means of determining the fuel flow to the ionizer, the efficiency could be determined easily from the ion current measurements.

Two methods of metering fuel flow have been tried, neither with spectacular success. The first method consists of putting a measured amount of fuel in the reservoir and keeping the conditions constant until the supply is exhausted. The average flow rate can then be determined, but

fuel flows are generally small and long operating times are required. The difficulties of keeping conditions absolutely constant during a long run are obvious. The second method utilizes the electrolytic diffusion of cesium through cesium glass (Ref 18, 74). This method should be very accurate since the fuel flow is determined from Faraday's law. The glass membrane through which the cesium diffuses has been found to break after only a few hours of use. If this difficulty can be overcome this method should prove valuable.

Another technique which appears promising is the direct measurement of the neutral fraction in the ion beam. A probe with a heated filament of oxidized tungsten is inserted into the ion beam and biased so as to repel ions. The neutral atoms in the beam can still strike the filament and be ionized by the high work function surface. By collecting the ion current from the probe one can determine how many neutral atoms are in that particular part of the beam. There are difficulties with photoelectric currents and secondary electron emission which still need to be solved.

None of these methods has been perfected, yet. Until a reliable technique is available, however, research on porous ionizers cannot proceed far.

V. Conclusions and Recommendations

The Saha-Langmuir equation in the form of equation (10) applies only to homogeneous (single crystal) surfaces with no adsorbed atoms. The modified equation for a patchy (polycrystalline) surface adequately explains the ionization of all alkali metals on tungsten, but fails to explain the data for platinum without the inclusion of some sort of reflection coefficient for incident atoms. Furthermore, the only reasonable explanation for these so called "reflection coefficients" is in terms of the energy band structure of the adsorbed atom-metal system. Hence, a full understanding of surface ionization awaits the formulation of a quantum-mechanical theory. Experiments on semi-conductors should be made in order to shed some light on this problem.

If the temperature of the surface is sufficiently low, a film of adsorbed atoms can form which drastically reduces the work function of the surface. Ion emission ceases completely if the work function gets far below the ionization potential of the adsorbed atoms. This critical temperature for ionization is a function of the rate at which atoms arrive at the surface and has only been determined experimentally for cesium, rubidium, and potassium on tungsten. A program to systematically test other combinations and determine their ionization efficiencies and critical temperatures is needed.

The choice of cesium and tungsten as the fuel and ionizer for ion propulsion is predicated mainly on a lack of information concerning other combinations. The porous plug emitter is considered necessary in order

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to avoid charge-exchange collisions in the ion acceleration region. Such collisions would result in the rapid sputtering away of electrode material by ion beam interception.

There exists practically no experimental data on the surface diffusion coefficients of the alkali metal elements on high work function surfaces. Therefore, it is difficult to predict the performance expected from porous ionizers.

The concept of critical temperature is slightly different when atoms are diffusing onto the surface from pores. The rise in ion current is expected to be less rapid in the critical temperature range than for surfaces where atoms are supplied uniformly. Furthermore, the equations for critical temperature, (24), (25), and (26), may be as much as 200-300 degrees too low when applied to porous ionizers. Experiments to confirm these equations for porous surfaces should be made.

Experimental data on porous ionizers are incomplete at present primarily due to the fact that there is no accurate, reliable way to determine the ionization efficiency of such a device. A method for accurately metering the fuel to a porous ionizer is urgently needed if research in this area is to be meaningful.

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Vita

Donald D. Mueller was born on [REDACTED], the son of Anton J. Mueller and Bonita B. Mueller. After completing his secondary education at [REDACTED], he attended Northwestern University, Evanston, Illinois, and the University of Illinois, Urbana, Illinois, where he was graduated with the degree of Bachelor of Science in Mechanical Engineering in June 1955 and received his commission as Lieutenant in the USAF Reserve.

He worked at the Flight Propulsion Laboratory of the General Electric Company until entering active duty in February 1956. He graduated from pilot training in April 1957 and was assigned to the Tactical Air Command as a fighter-bomber pilot until entering the Institute of Technology in August 1959.

Permanent address: [REDACTED]
[REDACTED]

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