

SURFACE IONIZATION

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INTRODUCTION

IN the phenomenon of surface ionization (SI) positive or negative ions are formed on the surface of a body from which atoms or molecules are evaporating. Positive surface ionization (PSI), which means the production of positive ions, was discovered in 1923.^{1,2} In 1934 Morgulis³ mentioned the possibility of the formation of negative surface ions. In this negative surface ionization (NSI) atoms with positive electron affinity capture electrons as these atoms evaporate from a surface. This effect was observed experimentally in 1935.⁴

Up to the present time more than 50 papers have been published on the subject of SI, as well as a large number in which SI is used to solve various physico-chemical, physical, and technological problems. However, many of the basic laws of SI are still not clearly understood. The only reviews of PSI⁵ and of NSI⁶ in any language appeared in 1948 in a publication with a relatively small circulation, and these are now out of date. Chapter VI of Reimann's monograph⁷ is also out of date. The long chapter on SI in Dobretsov's monograph⁸ is now incomplete since recent work has been done with more highly perfected experimental techniques. The advances in the investigation of SI have stimulated a critical review of previous results and of the organization of the experimental work. The critical examination of papers published in the field of SI may assist further work.

I. THE FORMATION OF POSITIVE SURFACE IONS. GENERAL IDEAS

1. Emission Equations for a Homogeneous Surface in the Absence of an Electric Field.

The quantitative parameters of SI are the degree of ionization

$$\alpha = \frac{n_+}{n} \tag{1}$$

and the ionization coefficient

$$\beta = \frac{n_+}{n_0} \tag{2}$$

Here n_0 is the atomic flux reaching 1 cm² of the surface per second; n_+ and n are the fluxes of positive ions and neutral atoms evaporating from

1 cm² of the surface in 1 second. In the steady state $n_0 = n + n_+$, so that α and β are related by

$$\beta = \frac{\alpha}{1 + \alpha}, \tag{3}$$

$$\alpha = \frac{\beta}{1 - \beta}. \tag{4}$$

The value of α depends on the work function ϕ and temperature T of the surface, on the atomic ionization potential V , and on the electric field E that accelerates the ions from the surface. In 1924 Langmuir and Kingdon derived an expression for α thermodynamically, in the absence of an electric field (α_0).⁹ Considering the thermodynamic equilibrium of a mixture of ideal atomic, ionic, and electronic gases on the surface of a metal, using a statistical expression for the equilibrium constant, and assuming that the equilibrium concentration of the electronic gas is determined by the thermionic emission of electrons from the metal, Langmuir and Kingdon found that

$$\alpha_0 = A \exp \frac{\epsilon}{kT} (\phi - V), \tag{5}$$

where $A = \frac{g_+}{g_0}$ is the statistical weight ratio of the ionic and atomic states of an adsorbed atom, ϵ is the ionic charge, and k is Boltzmann's constant. When the excitation level of the element or its ion is comparable with kT , instead of the statistical weight ratio $\frac{g_+}{g_0}$ in α we must use the ratio $\frac{Q_+}{Q_0}$ of the statistical sums,¹⁰ where

$$\left. \begin{aligned} Q_+ &= g_+ + \sum_j g_+^j \exp \left(-\frac{E_+^j}{kT} \right), \\ Q_0 &= g_0 + \sum_j g_0^j \exp \left(-\frac{E_0^j}{kT} \right). \end{aligned} \right\} \tag{6}$$

Here E_+^j and E_0^j are the energies of excitation to the j -th quantum state of the ion and atom, respectively. It is easily seen that when $E^j \gg kT$ the sums in Q_+ and Q_0 can be neglected, and the statistical sum ratio becomes the statistical weight ratio of the ionic and atomic ground levels. Equation (5) is usually called the Langmuir-Saha equation; for a given metal-atom system it describes the temperature dependence of the degree

of SI. Since $\ln \alpha_0 = \ln A + \frac{\epsilon(\varphi - V)}{kT}$, $\ln \alpha_0 = f\left(\frac{1}{T}\right)$ will be represented for $A = \text{const}$ by a straight line with the slope $\frac{\epsilon(\varphi - V)}{k}$, and the value of $\ln \alpha_0$ at $\frac{1}{T} = 0$ will determine $\ln A$.

In deriving (5) it has been assumed that the metal surface is uniform with respect to the work function, so that φ in (5) agrees with the thermionic work function.

Copley and Phipps studied the possibility of the elastic reflection of ions and atoms from a surface.^{11,12} Introducing the reflection coefficients r_+ and r_0 for ions and atoms, respectively, they obtained

$$\alpha_0 = \frac{1-r_+}{1-r_0} A \exp \frac{\epsilon}{kT} (\varphi - V). \quad (7)$$

Morgulis³ and Ansel'm¹³ were the first to use quantum mechanics in deriving expressions for α_0 ; the latter did not consider $A = \frac{g_+}{g_0}$. Avak'yants¹⁴

also obtained (5) by considering the contact between a metal and partially ionized vapor above it (a "gaseous semiconductor"). Sufficiently rigorous thermodynamic and statistical derivations of (5) are found in the monograph by Dobretsov.⁸

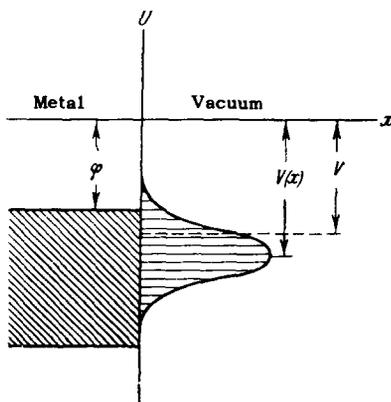


FIG. 1. Valence electron level of an atom close to a metal surface. $V > \varphi$.

According to the ideas of Gurney,¹⁵ which were applied to SI mainly by Dobretsov, the electronic energy levels of a metal and adsorbed atom form a single system. The valence-electron level V of an atom close to the metal surface is transformed into a quasi-continuous band, the maximum $V(x)$ of which is shifted from the discrete level V of the isolated atom (Fig. 1).¹⁶ The breadth of the band and the shift depend on the distance of the adsorbed atom from the surface; with increasing distance, $V(x)$ approaches V . For x of the order of atomic dimensions the atomic and ionic states of the adsorbed atom are indistinguishable because of the intense electron exchange between the adsorbed atom and the metal. When the electron is in the

region of the adsorbed atom the charge of the latter is zero; otherwise the charge is $+\epsilon$. The time-averaged charge of the adsorbed atom ranges from 0 to $+\epsilon$ for different interacting metal-atom systems, depending on the position of the adsorbed-atom band of levels with respect to the Fermi level.

If the adsorbed atom possesses positive electron affinity the foregoing discussion applies to the electron-affinity level of the atom. In this case the average charge of adsorbed atoms may be negative. With increasing x the probability of electronic transitions diminishes and vanishes at a certain distance x_0 . It was shown by Dobretsov^{8,25} that the degree of SI may be regarded as the product of two relative probabilities—the relative probability that an adsorbed atom will pass outside the critical distance x_0 for charge exchange as an ion or atom,

$\left(\frac{W_+}{W_0}\right)_{x_0}$, and the relative probability of evaporation as a ion or atom, $\left(\frac{W_{\lambda'_+}}{W_{\lambda'_0}}\right)$, since in evaporation the

work done to remove an ion or atom is λ_+ or λ_0 , respectively, when $E = 0$, and λ'_+ or λ'_0 when $E \neq 0$. Thus

$$\alpha = \left(\frac{n_+}{n}\right) = \left(\frac{W_+}{W_0}\right)_{x_0} \cdot \left(\frac{W_{\lambda'_+}}{W_{\lambda'_0}}\right) = W_1 \cdot W_2. \quad (8)$$

The relative probability of transforming an adsorbed atom into an ion at the distance x_0 is given by

$$\left(\frac{W_+}{W_0}\right)_{x_0} = A \exp \frac{\epsilon}{kT} (\varphi - V(x_0)). \quad (9)$$

The probability of evaporation, given a Maxwellian energy distribution of adsorbed atoms and temperature T equal to that of the metal, is proportional to $e^{-\lambda/kT}$; therefore

$$\left(\frac{W_{\lambda'_+}}{W_{\lambda'_0}}\right) = \exp \frac{\lambda'_0 - \lambda'_+}{kT}.$$

Then

$$\alpha = A \exp \frac{1}{kT} [(\varphi - V(x_0))\epsilon + \lambda'_0 - \lambda'_+]. \quad (10)$$

Dobretsov considered the circular process whereby a neutral atom at distance x from the metal is removed to $x = \infty$ and is there ionized; an electron is introduced into the metal; the ion returns to the distance x , where it is again transformed into an atom. He thus obtained^{17,18}

$$\epsilon[V - V(x_0)] = \lambda_+ - \lambda_0. \quad (11)$$

Then

$$\alpha = A \exp \frac{1}{kT} [\epsilon(\varphi - V) + (\lambda'_0 - \lambda_0) - (\lambda'_+ - \lambda_+)]. \quad (12)$$

In the absence of external fields $\lambda_0 = \lambda_+$, $\lambda_+ = \lambda_+$, and (12) agrees with (5)

The statistical derivation of (5) was subjected to criticism by Avak'yants,^{14,19,20,103} but a discussion with Dobretsov^{21,104} showed the objections of the former to be unconvincing.

It follows from the foregoing that since the position of the valence electron level with respect to the Fermi level in the metal varies with the distance x of the adsorbed atom from the surface, the time-averaged charge of adsorbed atoms on the metal surface will generally differ from that at the distance x_0 . The charge of adsorbed atoms at x_0 , averaged with respect to time or, equivalently, over all atoms, determines W_1 and α , since the average charge of adsorbed atoms on the surface at $x = 0$ determines the electric double surface layer. Therefore the degree of surface ionization α cannot indicate whether the adsorbed atoms on the surface are predominantly in an atomic or ionic state.

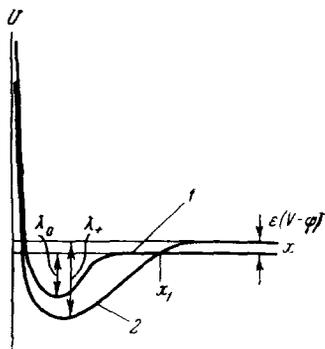


FIG. 2. Potential energy of the system consisting of the metal and an adsorbed atom: 1 - Atom-metal; 2 - Ion-metal.

To clarify the foregoing we represent the energy of interaction between an ion and atom of the surface by means of potential curves such as those given in references 20 and 22 (Fig. 2). The potential energy of the metal-atom system is reckoned from its value at $x = \infty$. Figure 2 corresponds to $V > \phi$; λ_0 and λ_+ are the heat of evaporation of the atom and ion, respectively. When $\lambda_+ - \epsilon(V - \phi) > \lambda_0$ the adsorbed atom on the surface will most probably be in the ionic state; in this case the average charge of adsorbed atoms on the surface will be close to ϵ , thus lowering the work function. Consequently, $V < \phi$ is not a necessary condition for the lowering of the metal work function by adsorbed atoms. On the other hand, the adsorbed atom will most probably be in the atomic state when its distance from the surface is $x > x_1$ (Fig. 2). Therefore α will be small despite the fact that adsorbed atoms on the surface are principally ionic. We may also consider the inverse case, in which $\lambda_+ - \epsilon(V - \phi) < \lambda_0$. Adsorbed atoms on the surface can now be principally atomic but considerable evaporation of ions can occur.

2. Emission Equations for a Homogeneous Surface in the Presence of an Electric Field

When an electric field is applied to the metal surface the thermodynamic equilibrium between the surface and adsorbed atoms may be disturbed. The same difficulty arises as in the proof of the Richardson-Dushman equation for thermionic emission of electrons in the presence of a field. The applicability of the Saha-Langmuir equation in the presence of a field at the surface can be decided only by experiment.

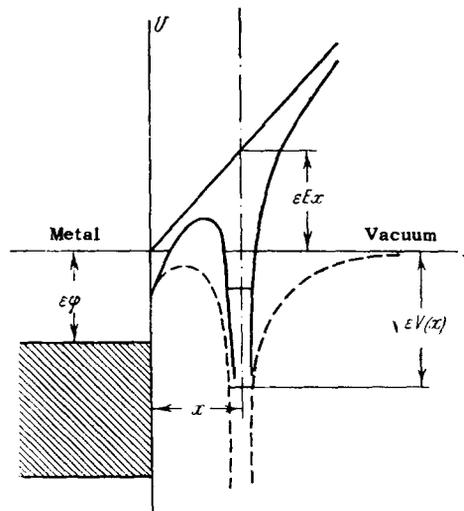


FIG. 3. Shift of valence-electron level $V(x)$ of an adsorbed atom in the presence of a strong uniform electric field E at the surface.

To derive an expression for α in the presence of an electric field at the surface, we must consider the following:

1. In a field E , as first noted by Morgulis,²³

the level $V(x_0)$ is shifted by the amount $\int_0^{x_0} E dx \cong Ex_0$

with respect to its position when $E = 0$ (Fig. 3).

2. As was pointed out by Dobretsov,²⁴ λ_+ is reduced in a field E by $\epsilon\sqrt{\epsilon E}$, since λ_+ includes the work required to overcome the electric image forces, and the external field pulls ions from the surface, thus reducing the attraction between an ion and the surface. The reduction of λ_+ can reach its limit $\frac{\epsilon^2}{4x_0}$ when the external field compensates the image force field at x_0 .

3. In an inhomogeneous field λ_+ and λ_0 increase by $\frac{1}{2} a_+ E^2$ and $\frac{1}{2} a_0 E^2$, respectively (a_+ and a_0 are the polarizability of the ion and atom, respectively).

Equation (12) now becomes²⁵

$$\alpha = A \exp \frac{\epsilon}{kT} \left[(\phi - V) + Ex_0 + \sqrt{\epsilon E} + \frac{E^2}{2\epsilon} (a_0 - a_+) \right], \quad (13)$$

since

$$\lambda'_0 - \lambda_0 = \frac{1}{2} a_0 E^2, \quad \text{and} \quad \lambda'_+ - \lambda_+ = \frac{1}{2} a_+ E^2 - \varepsilon \sqrt{\varepsilon E}.$$

The general equation (13) can be put into a suitable particular form depending on the range of variation of E . Thus, when E is less than 10^6 v/cm the terms $\varepsilon E x_0$ and $\frac{1}{2} E^2 (a_0 - a_+)$ can be neglected compared with $\sqrt{\varepsilon E} (a_0 - a_+ \cong 10^{-24} \text{ cm}^3)$, and x_0 , according to estimates, is of the order of the adsorbed-atom radius). Then

$$\alpha \cong A \exp \frac{\varepsilon}{kT} [\varphi - V + \sqrt{\varepsilon E}]. \quad (14)$$

In strong fields where $\varepsilon \sqrt{\varepsilon E} \geq \frac{\varepsilon^2}{4x_0}$, (13) becomes

$$\alpha = A \exp \frac{\varepsilon}{kT} \left[\varphi - V + E x_0 + \frac{\varepsilon}{4x_0} + \frac{E^2}{2\varepsilon} (a_0 - a_+) \right]. \quad (15)$$

Dobretsov suggests²⁵ that the last equation can be used to study ionization in ion guns where the field exceeds 10^8 v/cm and the surface temperature is low. Figure 4 shows the dependence on E of the separate terms in the exponential index of (13) (assuming $x_0 = 2 \times 10^{-8} \text{ cm}$ and $a_0 - a_+ = 10^{-24} \text{ cm}^3$).

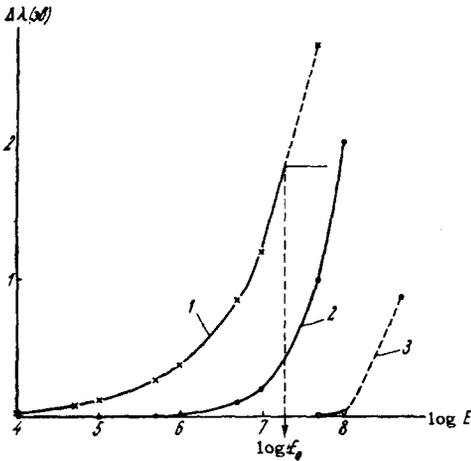


FIG. 4. Dependence of terms in (13) on E : 1) $\Delta\lambda = \varepsilon \sqrt{\varepsilon E}$;

2) $\Delta\lambda = \varepsilon E x_0$; 3) $\Delta\lambda = \frac{E^2}{2\varepsilon} (a_0 - a_+)$.

The study of surface ionization in strong fields is of interest in connection with the possibility of constructing ion sources and atomic detectors for practically any element regardless of its ionization potential. The investigation of SI in an electric field is very promising because it permits controlled variation of the exponential index in (13), which determines the degree of ionization.

From all of the foregoing considerations on which the derivation of (5) and (13) is based, it follows that these equations must apply to the evaporation of any adsorbed atom in temperature equilibrium with the surface. The previous history of the particles is therefore unimportant; they may

arrive either as neutral atoms or ions, or be produced by the dissociation of molecules arriving at the surface. However, in the SI of atoms n_0 is determined by the atomic or ionic flux to the surface and is independent of T , whereas in the ionization of molecules n_0 depends on T like the degree of molecular dissociation on the surface.²⁸ With respect to the SI of atoms belonging to the evaporating metal we must also take into account that $n_0 = f(T)$.⁸

When fast atoms or ions reflected from a surface retain a considerable fraction of their energy, $W_2 = 1$ in Eq. (8) at any surface temperature, and α_0 is given by (9),^{8,107} i.e.,

$$\alpha_0 = A \exp \frac{\varepsilon}{kT} [\varphi - V(x_0)]. \quad (16)$$

Ideas about electron exchange when fast ions interact with a surface are entirely applicable to ion conversion.¹⁰⁸

3. Surface Ionization of Atoms on Semiconductors

The foregoing discussion in connection with the derivation of (5) can be extended to semiconductors and dielectrics. Electronic levels are also collectivized when atoms are adsorbed on a semiconductor surface and electron exchange can also take place between an adsorbed atom and the semiconductor.

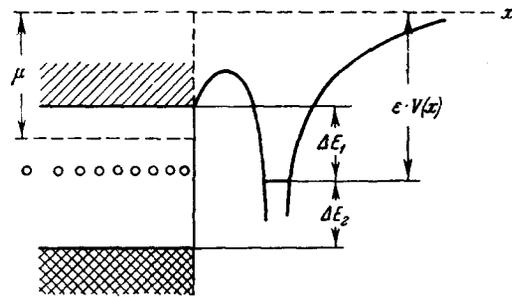


FIG. 5. Energy level scheme of a semiconductor-adsorbed atom system. μ is the electrochemical potential.

Morgulis²⁶ was the first to investigate qualitatively SI on semiconductors. When $V(x_0)$ of an atom is in an allowed semiconductor band, α_0 can be obtained by the method used for metals. When $V(x_0)$ equals a level of a forbidden or filled semiconductor band (Fig. 5) electron exchange will be inhibited. In the case of semiconductor temperatures $T > 0$, electron transitions can then occur to empty levels of the conduction band or to vacated levels of the filled band (in the first instance with an activation energy ΔE_1 , and in the second instance with an energy release ΔE_2). The probability and frequency of such transitions are much lower than for transitions between a metal and ad-

sorbed atom. Thus, we cannot use (5) when $\Delta E_{1,2} \neq 0$. The process bears a qualitative resemblance to nonresonant charge exchange of atoms and ions in the gaseous phase.

Avak'yants¹⁹ derived thermodynamically α_0 on the surface of an extrinsic semiconductor. The derivation differs from that for metals only in that the electron gas concentration above the semiconductor surface is calculated by thermionic-emission equations for semiconductors.

For SI on a n-type semiconductor we have

$$\alpha_0 = A_1(Q_+, Q_0, T, N) \exp \frac{e}{kT} (\mu - V), \quad (17)$$

and on a p-type semiconductor

$$\alpha_0 = A_2(Q_+, Q_0, T, N) \exp \frac{e}{kT} (V - \mu). \quad (18)$$

In (17) and (18) the coefficients A_1 and A_2 depend on T and on the impurity concentration N . Q_+ and Q_0 are the statistical sums of atomic and ionic states of the adsorbed atom, and μ is the electrochemical potential of the semiconductor.

The SI on semiconductors with known energy-level schemes has not yet been investigated experimentally, and the theory has therefore not been tested. The way in which an electric field would affect SI on semiconductors has not been discussed. It is obvious that such semiconductor properties as the energy-level shift in a field, or the field penetration into a semiconductor, must have an essential effect on the relationship between α and E .

4. Emission Equations for an Inhomogeneous Surface

A metal surface with an identical work function at all points could only be provided by the face of a perfect single crystal with no adsorbed atoms of other elements. It is also possible that the surface of a molten metal in a very high vacuum would be homogeneous with respect to the work function. The surfaces of the polycrystalline metals on which surface ionization is usually investigated are mosaics of different crystalline faces with different closeness of atomic packing and correspondingly differing work functions. The work functions of separate faces of metallic crystals have thus far not been measured with sufficient accuracy. Even for tungsten, which has been studied more than other metals, the work functions of different faces, obtained in different investigations, range from 4.6 to 6.0 eV for a (110) face and from 4.2 to 5.3 eV for a (116) face.²⁹ Thus the difference between the work functions on these two faces may possibly be as much as 1.8 eV. Ionization on polycrystalline metal surfaces cannot be represented by (5) and (13); this

fact was ignored in treating the results of the great majority of investigations of SI and has led to several erroneous conclusions. (5) has also been applied to obviously inhomogeneous surfaces, as in the SI of atoms on thoriated tungsten.

We regard the problem of SI on patchy surfaces as basic and shall discuss it more thoroughly.

As early as 1934 Dobretsov³² showed experimentally and later analytically¹⁰⁹ that, whereas electrons are emitted mainly from regions of an inhomogeneous surface where the local work function φ_k is small, ionization takes place mainly on regions of the surface with large φ_k . Thus when (5) and (13) are applied to inhomogeneous surfaces, φ differs in principle from the average thermionic work function. The ideas of Dobretsov remained undeveloped for a long time. In 1957 Romanov and Starodubtsev³³⁻³⁵ used the idea of a patchy surface to account for the results obtained in experiments on the ionization of Na and Li atoms on tungsten. Instead of directly considering SI on patchy surfaces, they attempted to find a distribution of patches on the W surface which would correspond with the observed curve of $n_+ = f(T)$. The SI on patchy surfaces in the absence of an electric field has been studied by Zemel³⁶ and for the general case in the presence of a field by the present authors.^{37, 38}

It is assumed that a patchy surface comprises a set of small areas F_k with work functions φ_k . Equation (5) is used to describe ionization from the surface of each patch and the ionization is summed over all patches just as is done for electron emission from patchy surfaces.^{39, 109} It is assumed here that emission from each patch is independent of the neighboring patches (fields and surfaces correspond to the normal Schottky effect). By means of this summation Zemel obtained the following expression for α_0 :³⁶

$$\alpha_0 = \left\{ \left(\sum_k \frac{F_k}{1 + \frac{g_0}{g_+} \frac{(1-r_0)}{(1-r_+)} \exp \frac{e(V-\varphi_k)}{kT}} \right)^{-1} - 1 \right\}^{-1}. \quad (19)$$

Here α_0 corresponds to the ion current obtained by extrapolating to the field $E = 0$. For a homogeneous surface only one term of the sum in (19) remains and the equation becomes identical with (7).

We shall now consider SI on patchy surfaces in the presence of a field, following references 37 and 38 and assuming $E > 10^4$ v/cm (the region of the normal Schottky effect). We shall obtain expressions for the experimentally determinable ion current I^+ from the surface. For a homogeneous surface it follows from (3) and (13) that

$$I^+ = \frac{\varepsilon F n_0 A}{A + \exp \frac{\varepsilon}{kT} (V - \varphi - \psi)}, \quad (20)$$

where

$$\psi = \sqrt{\varepsilon E} + E x_0 + \frac{E^2}{2\varepsilon} (a_0 - a_+).$$

In the particular case $\varepsilon (V - \varphi - \psi) \gg kT$, A in the denominator of (20) can be neglected for all practically possible values of T ; then

$$I^+ \cong \varepsilon F n_0 A \exp \frac{\varepsilon}{kT} (\varphi + \psi - V). \quad (21)$$

For a patchy surface (20) becomes

$$I^+ = \sum_k \frac{\varepsilon F_k n_0 A}{A + \exp \frac{\varepsilon}{kT} (V - \varphi_k - \psi)}. \quad (22)$$

It follows from (22) that the field increases the ion current from any patch, apparently increasing the work function for each patch by the same amount ψ . With rising T for $E = \text{const}$ the ionic emission of all patches for which $V - \varphi_k - \psi > 0$ must increase; conversely, for spots with $V - \varphi_k - \psi < 0$ the ionic emission decreases.

All patches on the surface will be divided into two groups. The group for which the relation $\varepsilon (V - \varphi_k - \psi) \gg kT$ is valid will be denoted by the subscript m , while all other patches will be denoted by the subscript i . By means of (21), Equation (22) then becomes

$$I^+ \cong \varepsilon A n_0 \left[\sum_m F_m \exp \frac{\varepsilon}{kT} (\varphi_m + \psi - V) + \sum_i \frac{F_i}{A + \exp \frac{\varepsilon}{kT} (V - \varphi_i - \psi)} \right]. \quad (23)$$

We shall apply (23) to special cases of SI, considering the following basic factors which can be investigated experimentally:

- 1) The temperature dependence of the SI current,
- 2) The dependence of I^+ on E ,
- 3) The possibility of determining $A n_0$.

a) The case of $\varepsilon (V - \varphi_{k \max} - \psi) \gg kT$. Equation (23) retains only the first sum, each term of which increases exponentially with T . Although the sum of the exponentials cannot be represented by a single exponential, $I^+ = f(T)$ can be represented by

$$I^+ = \varepsilon A^* \exp \frac{\varepsilon}{kT} (\varphi^* + \psi - V), \quad (24)$$

where

$$A^* = A n_0 \sum_m F_m \exp \frac{\varepsilon}{kT} (\varphi_m - \varphi^*). \quad (25)$$

Thus $\ln I^+ = f\left(\frac{1}{T}\right)$ will not generally be represented graphically by a straight line since $A^* = f(T)$. How-

ever, the dependence of A^* on the T is much weaker than that of the exponential term

$\exp \frac{(\varphi^* + \psi - V) \varepsilon}{kT}$, since the sum in (25) contains terms with exponential indices of different signs.

When $\ln I^+ = f\left(\frac{1}{T}\right)$ can be approximated by a straight line in a narrow temperature interval, its slope can be used to determine φ^* for that temperature range. The quantity φ^* can be called the effective work function of a patchy surface for ionization, and can be defined as the work function of the equivalent homogeneous surface for which the temperature dependence of the ion current in the given temperature interval has the same exponential form, except for a constant coefficient, as for a real patchy surface. The value of φ^* lies between $\varphi_{m \min}$ and $\varphi_{m \max}$ and depends on the areal ratio of patches with different φ_m .

Consequences of (24) and (25) are:

- 1) Extrapolation of the graphs of $\ln I^+ = f\left(\frac{1}{T}\right)$

for different temperature intervals enables us to obtain $\ln A^*$ for a given temperature interval. The product $A n_0$ cannot be calculated since the patch distribution on the surface is unknown.

2) φ^* and A^* are identical for elements with different ionization potentials V [subject to the condition $\varepsilon (V - \varphi_{m \max} - \psi) \gg kT$] in the same temperature interval. For this case (24) can be reduced to

$$I^+ = \varepsilon A n_0 \exp \frac{\varepsilon}{kT} (\psi - V) \sum_m F_m \exp \frac{\varepsilon}{kT} \varphi_m,$$

where the last sum, which takes patchiness into account, is identical for elements with different V . By measuring the current ratio $\frac{I_1^+}{I_2^+}$ for ele-

ments with ionization potentials V_1 and V_2 at the same T , in fields $10^4 < E < 10^6$ v/cm, we can determine the difference $V_2 - V_1$, since

$$\frac{I_1^+}{I_2^+} = \frac{A_1 n_{01}}{A_2 n_{02}} \exp \frac{\varepsilon}{kT} (V_2 - V_1). \quad (26)$$

- 3) $I^+ = f(E)$ can be represented by

$$I^+ = I_0^+ \exp \frac{\varepsilon}{kT} \psi, \quad (27)$$

where

$$I_0^+ = \varepsilon A^* \exp \frac{\varepsilon}{kT} (\varphi^* - V). \quad (28)$$

Since I_0^+ is independent of E , the graphs of $T \ln I^+ = f(\psi)$ for different T must be a set of parallel lines.

b) The case of $V - (\varphi_{k \min} + \psi) \leq 0$. Only the second sum remains in (23) and

$$I^+ = \varepsilon n_0 \sum_i \frac{F_i}{A + \exp \frac{\varepsilon}{kT} (V - \varphi_i - \psi)}. \quad (29)$$

In a limited range of T we can also replace (29) by the approximate equation

$$I^+ \cong \frac{\varepsilon n_0 F^*}{1 + \frac{1}{A^*} \exp \frac{\varepsilon}{kT} (V - \varphi^* - \psi)}, \quad (30)$$

which leads to an expression for the effective degree of ionization α^* of a patchy surface [see (3)].

$$\alpha^* = A^* \exp \frac{\varepsilon}{kT} (\varphi^* + \psi - V). \quad (31)$$

F^* in (30) represents the area of the effective emitting homogeneous surface, which may generally not coincide with the area F of a real patchy surface. The temperature dependence of α^* is determined mainly by patches with minimum φ_i . Therefore φ^* in (31) may be close to φ_e^* , the work function of a patchy surface averaged according to the thermionic electron current.

It follows from (29) that with increasing T the SI current falls off slowly. I^+ also depends only slightly on E . The current I^+ can vary only from $\varepsilon n_0 F$ to $\varepsilon n_0 F \frac{A}{A+1}$, since the exponential in (29) varies from 0 to 1 as T varies from 0 to ∞ .

When $\varepsilon (\varphi_{i \min} + \psi - V) \gg kT$ the exponential terms in the denominator of (29) may be neglected compared with A ; then

$$I^+ \cong \varepsilon n_0 F \quad (32)$$

and is practically independent of T and E in their possible ranges. In this case almost all atoms reaching the surface are ionized and n_0 can be obtained from I^+ . Equation (32) can be used to determine the temperature dependence of the vapor pressure of easily ionized elements and was first used by Langmuir and Kingdon for this purpose in the case of cesium.¹

c) The case of $\varphi_{k \min} + \psi < V < \varphi_{k \max} + \psi$. This is the most general case. The ion current is given by (23). With $\psi = \text{const}$, as T rises all terms of the first sum in (23) increase, while in the second sum some terms may increase and others decrease. Therefore I^+ may be either an increasing or decreasing function of T , depending on the ionization potential of the atom and the patch distribution on the surface. As E changes, the relationship of the terms of the sum may change; the current may therefore increase with temperature instead of decreasing, or vice versa.

In some special cases the complicated expression (23) may possibly be approximated in narrow temperature intervals by an exponential expres-

sion, and $\ln I^+ = f\left(\frac{1}{T}\right)$ may be represented with sufficient accuracy by a straight line with negative slope. In such cases we may also introduce the effective work function of the surface φ^* and compute I^+ from (24). But then, unlike (25),

$$A^* = A n_0 \left[\sum_m F_m \exp \frac{\varepsilon (\varphi_m - \varphi^*)}{kT} + \sum_i \frac{F_i}{A \exp \frac{\varepsilon}{kT} (\varphi^* + \psi - V) + \exp \frac{\varepsilon}{kT} (\varphi^* - \varphi_i)} \right]. \quad (33)$$

A^* here does not show a pronounced dependence on temperature. In general the graph of $\ln I^+ = f\left(\frac{1}{T}\right)$

for $\psi = \text{const}$ may depart from a straight line and be either concave or convex with respect to the horizontal axis, depending on the temperature dependence of A^* .

The following general conclusions are derived from (24) and (33):

1) When the graph of $\ln I^+ = f\left(\frac{1}{T}\right)$ enables us to obtain φ^* and A^* , the product $A n_0$ cannot be obtained.

2) The relation of increasing and decreasing terms in the sums of (23) and (33) depends on the ionization potentials of the atoms as well as on φ_k . Therefore, in contrast to the special case "a", in the general case φ^* and A^* differ when different elements are ionized on the same surface.

3) The ion current may be either an increasing or a decreasing function of T . Also, depending on the relative behavior of terms in the sums of (23) and (33), the decrease of I^+ as T increases may be followed by an increase.

4) It follows from (24) that as E increases the slope of $\ln I^+ = f\left(\frac{1}{T}\right)$ must decrease. If a rise of

E leads to a redistribution of increasing and decreasing terms in the sums the temperature dependence of the current will change and φ^* will diminish. Thus $\varphi^* = f(E)$. If A^* varies slowly with E , when $T = \text{const}$ $I^+ = f(E)$ may also be represented by (27) and (28) although the slope of $T \ln I^+ = f(\psi)$ will be smaller than in special case "a"; this occurs because with increasing E the denominators of all terms in the second sum of (33) increase, so that A^* decreases.

The review of SI on surfaces with an inhomogeneous work function may be briefly summarized as follows:

1. The Langmuir-Saha equation in the form (5) or (13) cannot be used to describe SI of atoms on patchy surfaces.
2. The temperature dependence of the SI

current in the case of polycrystalline metallic surfaces is determined by the effective work function φ^* of the surface. Then $\varphi^* = f(T, E, V)$ for a given surface and in principle does not agree with φ_e^* .

3. In surface-ionization experiments performed thus far on inhomogeneous surfaces, A^* was determined [Eqs. (25) and (33)] rather than $A^{11,12 40-47}$. These two quantities cannot justifiably be considered equal.

5. Thresholds in the Temperature Dependence of the Surface Ionization Current

In the foregoing discussion of SI it has been assumed that the degree of adsorptive coating of the surface by atoms of the element being ionized is small at all T ; thus only the inhomogeneity of the metallic surface is taken into account, independently of the temperature. Under this hypothesis, in the case of $\epsilon(\varphi_{k \min} + \psi - V) > 0$, it follows from (22) that the largest SI current, $\epsilon n_0 F$, will be observed when $T = 0$. When $\epsilon(V - \varphi_{k \max} - \psi) > 0$, the current must rise from $I^+ = 0$ at $T = 0$, with increasing surface temperature. However, as T is reduced under real experimental conditions, adsorption of ionized atoms on the metallic surface begins. φ_k is consequently modified and the foregoing equations cannot be used. In the ionization of the alkali metals Cs, Rb and K on a tungsten surface in the range $T \sim 800-1000^\circ\text{K}$ the ion current falls off sharply. The threshold ionization temperature T_0 at which a measurable ion current begins to be observed differs for different atom-surface combinations, because with a constant atomic flux n_0 to the surface this temperature is determined by the heat of evaporation l of adsorbed atoms from the surface.

The concentration N of adsorbed atoms on the surface at temperature T is related to the atomic flux n_0 in the steady state by⁸⁵

$$n_0 = N \left(C \exp \frac{-(l_+ - \psi_1)}{kT} + D \exp \frac{-(l_0 + \psi_2)}{kT} \right),$$

where C and D are coefficients which depend slightly on the temperature, l_+ and l_0 are the isothermal heats of evaporation of an ion and atom, respectively, and ψ_1 and ψ_2 are corrections to the latter in the presence of an electric field at the surface. Thus $N = f(n_0, l_+, l_0, E, T)$.

If the range of the field is limited to $E \cong 10^6$ v/cm we have

$$n_0 = N \left(C \exp \frac{-(l_+ - \epsilon \sqrt{\epsilon E})}{kT} + D \exp \left(-\frac{l_0}{kT} \right) \right). \quad (34)$$

The first term of the sum in (34) characterizes

the rate of evaporation of adsorbed atoms in the ionic state, while the second term corresponds to the atomic state. At lower T it follows from (34) that when $n_0 = \text{const}$, N , and therefore the degree of coating θ of the surface by adsorbed atoms, will increase and the conditions of ionization on the surface will vary continuously. In the ionization of alkali metal atoms on W an increase of θ leads to a reduction of φ_k .

When $(V - \varphi_{k \min} - \psi) < 0$ a reduction of φ_k induces a reduction of I^+ [see (29)], although a decrease of T when $\varphi_k = \text{const}$ must lead to a slow rise of the current I^+ . Consequently at some temperature I^+ passes through a maximum, after which it begins to fall off sharply, since N and θ depend exponentially on T . With a small reduction of T the decrease of φ_k is so great that the condition $(V - \varphi_{k \min} - \psi) < 0$ may become $(V - \varphi_{k \max} - \psi) < 0$. When $T = T_0$ we have $\theta \approx 1$ for the degree of coating, and the ionization threshold is observed. For a given combination of metal and adsorbed atom T_0 naturally depends on n_0 and E . It follows from (34) that as n_0 increases (for $E = \text{const}$) T_0 also increases, whereas it decreases as E becomes larger with $n_0 = \text{const}$.

If $(V - \varphi_{k \min} - \psi) < 0$ adsorbed atoms evaporate mainly in the ionic state. Then the second term in (34) may be neglected, leaving

$$n_0 \cong NC \exp \frac{-(l_+ - \epsilon \sqrt{\epsilon E})}{kT}. \quad (35)$$

This last equation assumes a small degree of coating of the surface and therefore in general describes the conditions for evaporation corresponding to the beginning of the decreasing current range. For large θ it can represent the conditions for evaporation on portions of the surface which are not covered with adsorbed atoms. Experiments with electron and ion guns indicate that when $\theta < 1$ adsorbed atoms are distributed on the surface mainly in patches.

It can be assumed that with a shift of the threshold, resulting from a change of n_0 or E , equal currents in the near-threshold region correspond to equal N and θ ; then with $I^+ = \text{const}$ and $n_0 = \text{const}$ (35) leads to

$$\frac{l_+ - \epsilon \sqrt{\epsilon E}}{kT_0} = \text{const}. \quad (36)$$

Thus the threshold temperature must decrease linearly with increasing \sqrt{E} .

When $(V - \varphi_{k \max} - \psi) > 0$ an increase of N and θ , leading to a reduction of φ_k , induces a steeper current drop than would follow from

(24). The threshold values of T also increase with n_0 , but, unlike the preceding case, are practically independent of E , since for any θ adsorbed atoms evaporate mainly in the atomic state and $n_0 \cong ND \exp\left(-\frac{I_0}{kT}\right)$, with I_0 independent of E in the given field range.

Temperature thresholds of ionization must also be observed in the general case $\varphi_k \min + \psi < V < \varphi_k \max + \psi$. The variation of T_0 as a function of E may here resemble each of the foregoing special cases, depending upon which of the sums in (23) is dominant. The redistribution of increasing and decreasing terms in the sums of (23) as E increases may result in a relatively larger shift of T_0 for large E .

II. EXPERIMENTS ON POSITIVE SURFACE IONIZATION

During the thirty-five years since its discovery, surface ionization has been studied not only for the purpose of determining the fundamental physical laws which underlie it but also for the purpose of its application to a number of physico-chemical and practical problems. Among these we may mention first the use of SI to study the physico-chemical characteristics of adsorbed metal coatings, the determination of atomic constants (V , I_0 , I_+ and the electron affinity ϵS), and the use of SI to produce ion sources and sensitive indicators of weak molecular and atomic beams.

In the present review we shall be concerned mainly with investigations of the physical laws of SI.

6. Technique of Investigating Positive Surface Ionization (PSI)

The PSI of alkali metals on the surfaces of high-melting metals, especially polycrystalline tungsten, has been investigated most completely. With regard to homogeneous surfaces we have only one qualitative observation of sodium-atom ionization on separate faces of a tungsten single crystal, undertaken to determine the work function on the (110) face.⁴⁸

Most experiments have investigated the temperature dependence of the current $I^+ = f(T)$, for comparison with (5), which is valid only for homogeneous surfaces. The functional relationship $I^+(E)$ has also been studied and the discrepancy between the experimental and theoretical values of A has been discussed for a long time.

The experimentally measured quantities are I^+ , n_0 , T , φ and E . The reliability of the experimental

results naturally depends on the accuracy with which these quantities are determined.

The simplest experimental apparatus for the study of PSI is a cylindrical diode in which the heated filament is the ionizing surface. The collector surrounding the filament usually is divided into three cylinders coaxial with the filament, the middle cylinder being used for measurements and the others as guard rings. Electrons or positive ions will flow to the collector from the filament, depending on the sign of the potential difference between them. A suitable instrument in the filament-collector circuit measures the ion current $I^+ = \epsilon n_+$ from the filament combined with the current of photoelectrons from the inner surface of the cylinder to the filament and of secondary electrons ejected from the collector by the positive ions. Since the photo-current rises rapidly with the filament temperature and secondary emission increases with the electric field, the experimental relationships $I^+ = f(T)$, $I^+ = f(E)$ and values of n_0 may be far from accurate in the absence of reliable means to inhibit secondary currents. With high metal vapor pressure in the enclosure the current I^+ is also affected by processes associated with the passage of current through the gas.

It is most difficult to determine n_0 experimentally. Atoms can be supplied to the filament in two ways—from the vapor or in the form of a molecular beam. All early experiments on SI of alkali metals employed the vapor or “bulb” method. A small quantity of alkali metal purified by vacuum distillation was introduced into the evacuated bulb, which was heated in a thermostatic oven to the temperature t in order to reach the required vapor pressure of the alkali metal. This procedure is suitable only for volatile elements. If the relation between the vapor pressure p and the temperature t of the thermostatic oven is known it is easy to compute $n_0 = f(t)$ from the equations of the kinetic theory. However, $p = f(t)$ for alkali metals is known only to within a few dozen percent, and the values of n_0 obtained in this manner are therefore very unreliable, with consequently incorrect values of the ionization coefficient β . Absolute values of n_0 are not required to determine the functions $I^+ = f(T)$ and $I^+ = f(E)$; it is only required that n_0 remain constant during measurements. This means that the thermostatic-oven temperature must be carefully maintained constant, because the vapor pressure of alkali metals depends strongly on t . It must also be remembered that when the filament temperature T varies over a wide range there is a change in the thermal conditions of the apparatus and thus in

the number of atoms evaporated from the surface of the measuring cylinder and other parts of the apparatus. This has usually not been taken into account, although it is necessary to do so even when a filament of small diameter is used.

In the molecular beam method, which was first employed in references 32 and 11, vapor of the test element leaves a special furnace through a small aperture, passes through a system of defining slots and reaches the filament as a narrow ribbon-like beam. Suitable slot dimensions in the measuring cylinder prevent the beam from striking the walls of the cylinder while passing through it. The path of the beam to the filament can be interrupted and opened at will by means of a special shutter. The determination of I^+ as the difference between readings without and with interruption of the beam thus excludes the photocurrent effect to a considerable degree as well as the influence of additional heat emission from the filament on the magnitude of n_0 . On the other hand, the distortion of $I^+ = f(E)$ is fully retained in the molecular beam technique unless special steps are taken to hold back secondary electrons on the cylinder surface. This can be accomplished by means of an axial magnetic field, first introduced by Morgulis,²³ or by special highly transparent grids to retard the secondary electrons.³⁷ We believe that the second of these procedures is much more reliable than the first.

The temperature T of the tungsten filament is determined either by means of an optical pyrometer or, as in the majority of PSI experiments on tungsten, from tables⁴⁹⁻⁵¹ relating filament temperature and current. But it must be remembered that the tables pertain only to tungsten of very high purity, which had previously been subjected to very definite heat treatment.⁵¹ For ordinary commercial tungsten the discrepancy between the pyrometric and tabular temperatures may be as much $\sim 200^\circ$.⁵³ This was first noted by Meyer,⁵² but was ignored in most later work. In studying PSI by the bulb method it is also necessary to take into account the radiation from the thermostatic oven, especially at low T .⁴²

In all experiments on PSI, φ was determined either from tabular data obtained from the slopes of the Richardson-Dushman curves for thermionic currents, or directly with the given experimental apparatus. It was shown by Dobretsov¹⁰⁹ and by Herring and Nichols³⁹ that for a surface with a nonuniform work function the Richardson-Dushman curves give the work function φ_e^* averaged for the electron current:

$$I_e = \sum_k B_k F_k T^2 \exp \frac{e}{kT} (V_{\pm E} - \varphi_k) \\ = B^* T^2 \exp \frac{e}{kT} (V_{\pm E} - \varphi_e^*) \dots \quad (37)$$

Here B_k is the thermionic emission constant of the k -th patch with the work function φ_k , I_e is the electron current emitted by the surface and

$$B^* = \sum_k B_k F_k \exp \frac{e}{kT} (\varphi_e^* - \varphi_k) \dots \quad (38)$$

E can be computed from the formula for a cylindrical capacitor but must be checked experimentally for agreement with the true value of E , because of possible roughness of the filament surface. There is no direct means of performing this check, but it can be done indirectly through measurement of the Schottky electron effect. Agreement between the geometric coefficient k obtained thereby and that calculated from the equation $E = ku$, where u is the applied potential difference between the filament and ion collector, provides some assurance that the filament surface lacks sharp points and that the determined filament temperature is correct.

7. Positive Surface Ionization of Cs, Rb and K Atoms on Tungsten in Weak Electric Fields

The ionization potentials of cesium, rubidium and potassium atoms are 3.87, 4.10 and 4.32 v, respectively. For tungsten, as already indicated, $\varphi_k \min = 4.2 - 4.4$ v, and $\varphi_k \max$ is in the range 5.3-6.0 v. Therefore, although PSI of Cs, Rb and K on polycrystalline tungsten should be represented by the general equations (22) or (23), it can be expected that $I^+ = f(T)$ for these elements will be represented approximately by (29) or (30). This approximation is best justified for the ionization of cesium on tungsten.

The positive surface ionization of Cs, Rb and K on polycrystalline tungsten has been investigated for a long time and with the greatest thoroughness.^{1,9,52,54-59,42,11,40,12} Some experiments have been performed on other polycrystalline surfaces (Mo, Ta⁵², and Re⁴²). We shall consider the surface ionization of alkali metals on platinum in another section of this article.

In early work, which was performed by means of the bulb method, the temperature range extended only from the initial appearance of an ion current up to $\sim 1700^\circ\text{K}$. At higher T the photocurrent from the collector became significant.

Figure 6 shows a typical curve of the ion current vs. temperature. Beginning at $T = 1200 - 1300^\circ\text{K}$ the observed relation $I^+ = f(T)$ agreed

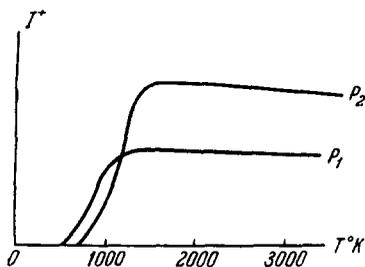


FIG. 6. $I^+ = f(T)$ for the ionization of C_s atoms on W .⁹ Vapor pressure $p_2 > p_1$.

qualitatively with (5), (7), and (30); the current was either independent of temperature or diminished slightly as the temperature rose. In agreement with Sec. 5, observations revealed a sharp falling-off of the ion current at low temperatures, ionization thresholds, and a shift of the threshold temperatures with variation of the alkali-metal vapor pressure. In early work experimental results could not be compared quantitatively with theory; however, this was done by Copley and Phipps.^{11,12,40}

Copley and Phipps investigated the ionization of K on pure and oxidized tungsten by the molecular beam method and measured $I^+ = f(T)$ up to $T = 2800^\circ K$. On the basis of the vacuum conditions and aging of the apparatus in these experiments the surface could be regarded as free of adsorbed atoms. The value of n_0 was determined from the ion current from an oxidized filament assuming 100 percent ionization on the latter (vaporization was identical for current measurements from both a pure tungsten and oxidized filament). The values of n and

$\alpha = \frac{n_{\pm}}{n}$ were obtained from the current difference $I_{W-O}^+ - I_W^+$. Figure 7(1) shows the relation

$\log \alpha = f\left(\frac{1}{T}\right)$ that was observed. The experimental values were well fitted by the straight line (1) on the segment represented by a solid

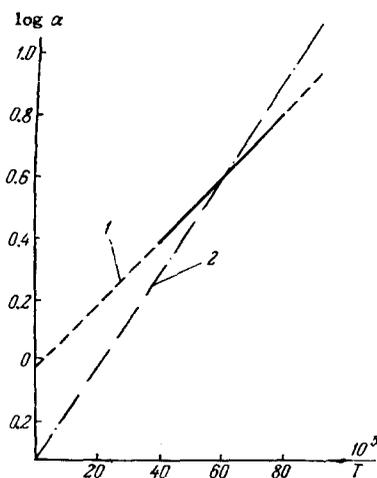


FIG. 7. $\log \alpha$ vs. $1/T$ in the ionization of potassium on tungsten.¹² $F = 3350$ v/cm.

line. From the slope of this straight line extended to $E = 0$, and by using (5), they obtained $\phi = 4.52$ v. [They also give the more general equation (7), but, citing reference 59, they assume $\left(\frac{1-r_+}{1-r}\right) = 1$.] The value obtained for ϕ is close to ϕ_e^* for tungsten. Therefore Copley and Phipps have suggested that the determination of ϕ from the slope of $\log \alpha_0 = f\left(\frac{1}{T}\right)$ is an independent means of determining the work function of a surface. They extrapolated $\log I^+ = f\left(\frac{1}{T}\right)$ to

$T = \infty$, obtaining $A \cong 1$ instead of the theoretical value $A = 1/2$ (straight line 2 in Fig. 7). They, as well as Reimann,⁴¹ accounted for this discrepancy by suggesting that the temperature dependence of the work function of tungsten has the form $\phi = \phi_0 + \gamma T$. Different values of γ were obtained when different elements were ionized on W in the same temperature range.⁴⁴

We make the following comments on the work of Copley and Phipps:

1. The hypothesis that the entire tungsten surface is oxidized and that $\beta = 1$ when potassium is ionized on oxidized tungsten, as well as the hypothesis that at $T = 1640^\circ K$ (the control point) the surface is free of an oxygen coating, requires proof. Since $n = n_0 - n_+$ is small when potassium is ionized on tungsten, errors in determining n_0 and n_+ result in large errors for n and α_0 .

2. Equation (5) cannot be used to represent PSI on polycrystalline tungsten. These investigators determined the temperature dependence $\alpha_0^* = f(T)$ to be given by (31). Their value for A^* must differ from $A = \frac{g^+}{g_0}$; thus their calculation for the temperature coefficient of the work function of tungsten has not been justified.

8. Positive Surface Ionization of Na and Li on Tungsten in Weak Fields

The ionization potentials of Na and Li are 5.14 and 5.40 v, respectively; therefore when they are ionized on tungsten we have $\phi_e^* < V$. However, we must take into account the inhomogeneity of the work function of polycrystalline tungsten as well as the fact that the work function on a (110) face according to various investigations may be as much as 6 v and may thus possibly exceed the ionization potentials of Na and Li. Ionization on this face may make the principal contribution to ion emission, especially at low T , if, of course, this face does not occupy too small an area on the

surface. In this case we must therefore use the general emission equation (23), while (24) is only a rough approximation that is more accurate for Li than for Na. The first investigations of PSI of sodium on tungsten were reported in references 23, 32 and 42. Morgulis²³ experimented with Na vapor but used an axial magnetic field to suppress the current of photoelectrons. Dobretsov³² used the molecular beam method so that his results are practically free of photoelectronic interference. The vacuum conditions in the experiments of both investigators could not guarantee the absence of surface contamination by gases containing oxygen, at least in the temperature range up to 1700–1800°K.

By plotting $\log I^+ = f\left(\frac{1}{T}\right)$ for sodium ionization on tungsten Dobretsov obtained $\phi - V = -0.56$ v, which yields $\phi = 4.58$ v, thus practically agreeing with ϕ_e^* . Such good agreement, contrary to the theoretical predictions for ionization on patchy surfaces, may be due either to incorrect determination of filament temperatures from the tables or to the fact that the field E at the filament was small and the anomalous Schottky effect has occurred and smoothed out the inhomogeneous patchiness of the surface work function. Indeed, it was noted in later papers^{60,61,33,37} that for sodium ionization on tungsten ϕ^* exceeds ϕ_e^* considerably.

The curve $\log I^+ = f\left(\frac{1}{T}\right)$ for sodium ionization on tungsten at temperatures < 1700°K is not monotonic. It is shown in later papers^{31,33} that as the vacuum in the apparatus is improved the observed ion current maximum degenerates into a plateau that represents slight current variation for $T = 1200\text{--}1700^\circ\text{K}$ (Fig. 8). This plateau can easily

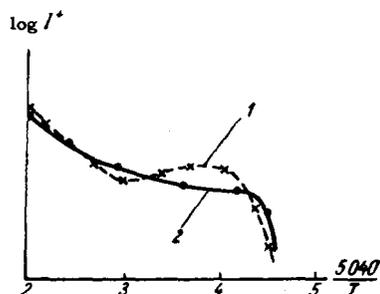


FIG. 8. $\log I^+ = f\left(\frac{1}{T}\right)$ for Na ionization on W.³³ Residual gas pressure in apparatus: 1) 10^{-6} mm Hg, 2) 10^{-7} mm Hg.

be accounted for by the natural inhomogeneity of the work function.³³ Cs, Rb and K impurities in sodium may also distort the curve of $\log I^+$

$= f\left(\frac{1}{T}\right)$ for $T < 1700^\circ\text{K}$. Figure 9 gives computed plots of $\log I^+ = f\left(\frac{1}{T}\right)$ for Na ionization on an ideal homogeneous metal surface with $\phi = 4.5$ v (curve 1), for 1% potassium impurity (curve 2) and the

combined ionization curve (3) representing the logarithm of the sum of ion currents from the sodium and the potassium impurity. Curve 3 reveals the characteristic plateau.

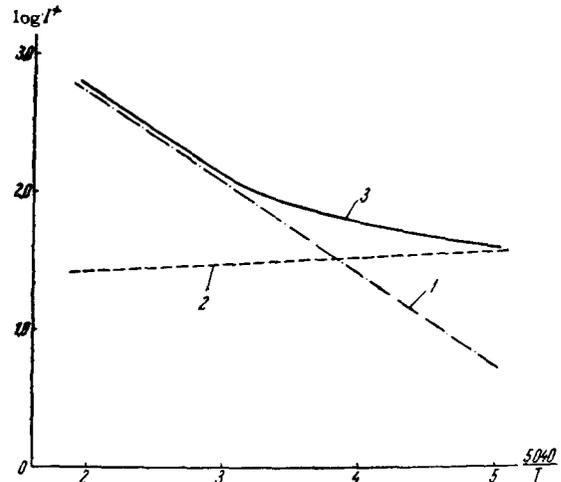


FIG. 9. $\log I^+ = f\left(\frac{1}{T}\right)$ for the ionization of sodium with 1% potassium impurity on a homogeneous surface with $\phi = 4.5$ v.

Romanov and Starodubtsev³³ investigated PSI of Na on W by the bulb method for T up to 2100°K (photocurrents could not be entirely eliminated by means of an axial magnetic field at higher temperatures), and by the molecular-beam method up to 2500°K. Their vacuum was better than that in earlier works, and they showed convincingly that the absolute values of the ion currents at $T > 1200^\circ\text{K}$ were higher than the values computed by means of (5) using $\phi = \phi_e^*$. The results were correctly interpreted on the basis of the naturally inhomogeneous work function of a polycrystalline tungsten filament. Assuming a definite patchy surface they obtained a $\log I^+$ vs $\frac{1}{T}$ curve that closely resembled the experimental curve. However, the assumed patch arrangement may not correspond to the real one because of a) possible errors in measuring currents and temperatures (secondary currents were not entirely excluded and the temperatures of filaments with silicon-alkali admixtures were obtained from tables), b) insufficiently strong fields at the filament surface (the region of the anomalous Schottky effect, so that emission from individual patches could not be regarded as independent of neighboring patches, and c) a small amount of potassium impurity in the sodium.

Dobretsov also investigated PSI of sodium on molybdenum and thoriated tungsten.^{32,62} The results for Mo were similar to those obtained for PSI on W. These investigations for Na on W-Th showed convincingly that ionization on a patchy

surface takes place mainly on spots with large ϕ_k . This was clearly demonstrated for a W-Th surface by Morgulis in 1940 using a cylindrical ion gun.⁶³ However, as already mentioned, the proper conclusions were not drawn from this work in the subsequent investigations of PSI on complicated surfaces.

Romanov and Starodubtsev^{64,34} have studied PSI of Li on polycrystalline W. In their earlier paper⁶⁴ these authors regarded (5) as applicable, but the technique and results in reference 34 are similar to those in reference 33, and the entire discussion in the latter paper may also be applied to reference 34.

9. Positive Surface Ionization of Alkali Halide Molecules on Tungsten in Weak Fields

The PSI of alkali halides has been investigated by Phipps and his coworkers,^{65,43,44} by Starodubtsev,^{66,28} and by others. The measured temperature dependence of the ion current $I^+ = f(T)$ of many salts at high temperatures was found to be similar to that for the corresponding alkali metal atoms. Figure 10 shows typical $I^+ = f(T)$ curves for the ionization of potassium and potassium halides on W which was measured by the molecular beam method.⁶⁷ A comparison of the curves for K and KX ionization shows that in all cases ionization begins at practically the same surface temperature T_0 , rises sharply with temperature, reaches a maximum at 1200 or 1300°K and then slowly declines. When KX molecules are ionized in the range from 1200° to 1700 or 1800°K the current diminishes more slowly as the temperature rises than when potassium atoms are ionized.

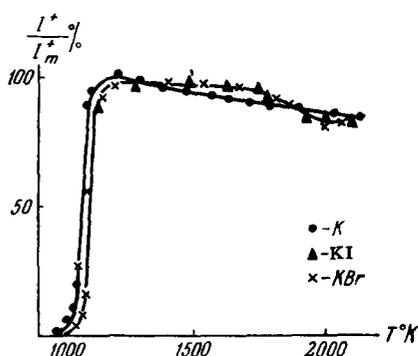


FIG. 10. Ionization of K atoms and KI and KBr molecules on tungsten.⁶⁷

Starodubtsev⁶⁶ and Zimm and Mayer⁶⁸ found the same value of the coefficient β for atoms and molecules within the limits of experimental error. Mass-spectrometric analysis of the positive ions showed that when the salts are ionized only atomic ions of the alkali metal are produced,⁶⁰ just as in the case of alkali atoms.

The experimental results suggest that at ionization temperatures the molecules are completely dissociated into atoms on a tungsten surface. Atoms of the alkali metal and halogen are bound to the surface by adsorption forces, but interact very weakly among themselves when the surface is covered to only a small degree. A sharp reduction of the ion current in the region of threshold T can be accounted for by the formation of either a W-M layer in the case of alkali metal ionization, or of a W-X-M layer in the case of the halide molecules, with a low value of the work function. The difference between the ionization curves of the metal and of the molecules from 1200 to 1800°K may result from the fact that at these temperatures halogen atoms are still held on the surface forming a W-X double layer with a higher work function than for pure tungsten. When $T > 1800^\circ\text{K}$ halogen atoms (with the probable exception of fluorine, which remains on W to higher temperatures) escape from W practically completely and the ionization of the halides obeys the same laws as those for the ionization of free alkali atoms.

We shall see that experiments on NSI of the salts confirm the catalytic effect of the W surface on the degree of dissociation of MX molecules. In some investigations of SI the salts were used as sources of alkali metal or halogen atoms.

10. Positive Surface Ionization of Alkali Metal Atoms and Alkali Halide Molecules on Platinum in Weak Fields

The PSI of alkali metal atoms on Pt was studied in references 31 and 61, that of alkali halides in reference 69. For platinum $\phi_e^* \cong 5.5$ v, which is above the ionization potentials of all alkali metals. Values of ϕ_k for separate faces of crystalline Pt are unknown.

It was found that the ion current in PSI on Pt is considerably below that given by (5), especially in the ionization of alkali halides (Figs. 11 and 12); β decreases as the vapor pressure of the alkali metal rises. We may expect $\phi^* > \phi_e^*$, and possible secondary effects at the electrodes can raise the measured currents above the true ones; therefore the observation of very low ionization coefficients of alkali metals on Pt may be attributed to properties of the platinum surface with respect to the adsorption and ionization of alkali metals. The authors of the references cited here use different physical hypotheses to explain their results.

Kim Heng Pong and Sokol'skaya, who observed higher threshold temperatures for the ionization of Na on Pt than on W, suggested that the heat

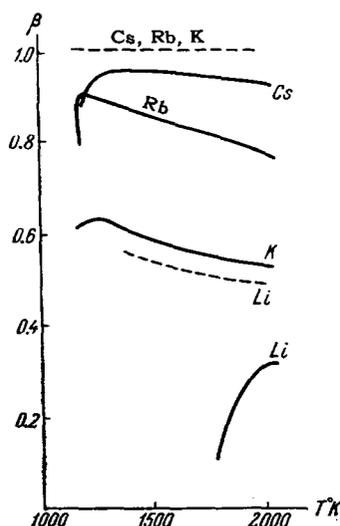


FIG. 11. Ionization of Li, K, Rb and Cs atoms on Pt. The dashed curves were calculated.⁶¹

of adsorption of Na on Pt is very high and that the Na layer remains on platinum up to temperatures at which intense evaporation of the Pt takes place; moreover, the adsorption of Na on Pt has the character of chemisorption and the Pt-Na layer possesses semi-conducting properties. As already mentioned in Sec. 3, when the valence electron level lies in a forbidden semiconductor zone, ionization is unlikely even if large values are found for φ_e^* .

Datz and Taylor performed their experimental work very carefully using high-purity platinum and the molecular beam method. To account for the low values of β they have suggested that there is considerable reflection of particles reaching the Pt surface. By introducing the reflection coefficient r_i they changed (7) to

$$\beta = \frac{n_+}{n_0} = (1 - r_i) \left[1 + \frac{g_0}{g_+} \frac{(1 - r_0)}{(1 - r_+)} \exp \frac{\varepsilon}{kT} (V - \varphi) \right]^{-1}. \quad (39)$$

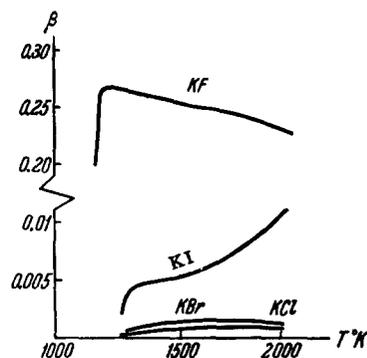
In the opinion of these authors high-values of r_i must either correspond to a very low heat of adsorption of atoms on the metal surface, which disagrees with the hypothesis of Kim Heng Pong and Sokol'skaya,³¹ or we must acknowledge a small probability of electron transitions in the platinum-adsorbed atom system. Figure 11 shows that this probability decreases as we pass from Cs to K.

In PSI of potassium halides on Pt the coefficients r_i reached 99% for KCl and KBr and about 75% for KF, so that β is very small in the ionization of these salts on platinum. PSI on platinum obviously requires further investigation.

11. Surface Ionization of Other Elements and Compounds in Weak Electric Fields

Many experiments have shown that other elements and compounds can also ionize on a surface with the production of atomic ions.^{10, 70-72, 74-77, 105}

FIG. 12. Ionization of potassium halides on Pt.⁶⁹



These investigations were usually not very detailed and we shall limit ourselves mainly to a brief enumeration. Most of the work was done on PSI of alkaline earth metals and some rare earths.^{70, 110-112}

The PSI of Ba on W ($V = 5.19$ v) was studied in references 71 and 72, and especially carefully by Morozov.¹⁰ In reference 72 it was observed that Ba ionization on W is not temperature dependent in the range $T = 2000$ to 2600°K ; this was there interpreted as indicating 100% ionization. However, it is possible that the Ba was insufficiently pure and contained alkali metal impurities; the apparatus may also have contained traces of oxygen. Morozov¹⁰ in treating his results by means of (5) took into account the statistical sums corresponding to excited states of Ba atoms and ions. The slope of the theoretical straight line $\log I^+ = f\left(\frac{1}{T}\right)$ gives $V - \varphi = 0.54$ v, whereas the experimental value was 0.39 v. This discrepancy can be accounted for by the patchiness of the W work function. From the data obtained by Morozov we may infer that $\varphi^* = 4.8$ v in his experiments with Ba ionization on W.

In reference 73 it was suggested that beams of Li atoms could be detected by means of SI on W, against which a continuous stream of oxygen is directed to insure sufficiently rapid oxidation of tungsten at high temperatures. Using this means of raising the work function of the surface, Szhenov observed the PSI of Ca ($V = 6.09$ v), Mg ($V = 7.61$ v) and Sr ($V = 5.67$ v).⁷⁴

Reference 75 reported extremely large ion currents from the ionization of Ca and Mg on tungsten in the presence of oxygen. The current density was as high as 5 or 6 ma/cm². The authors suggested that under their experimental conditions a layer of oxides of the ionized elements was formed on the W surface, and they compared their results with those obtained by means of (5) assuming $\varphi = \varphi_e^*$, although this is impermissible. In later work by the same investigators⁷⁶ employing an improved mass-spectrometric technique for measuring ion

currents, it was shown that the large currents reported in reference 75 may have resulted from the presence of alkali metal impurities in Mg and Ca. Special experiments reported in reference 76 also showed that when $T > 1800^\circ\text{K}$ MgO decomposes on a tungsten surface. The principal results in reference 76 were the detection of considerable ionization of Mg atoms on W only at high temperatures of the latter and the exponential temperature dependence of the ionization coefficient. $\phi^* \sim 4.8$ v from the data for the ionization of Mg on W.

Bakulina and Ionov⁷⁷ investigated the temperature dependence of PSI of uranium atoms on W when molecules of UCl_4 and UF_4 were ionized. A comparison was made with analogous results for Li from the ionization of LiCl and LiF . The simultaneous evaporation of uranium and lithium salts on a tungsten filament and a mass-spectrometric technique for separate measurements of U^+ and Li^+ ion currents enabled these investigators to obtain the difference between the ionization potentials of uranium and lithium from the temperature relationship $\log \frac{I_1^+}{I_2^+} = f\left(\frac{1}{T}\right)$ [Eq. (26)]. Using

5.40 v as the ionization potential of Li, $V = 6.08 \pm 0.08$ v was obtained for uranium. We note that when $(V_2 - V_1)$ is determined from the temperature dependence of $\log \frac{I_1^+}{I_2^+} = f\left(\frac{1}{T}\right)$ (Fig. 13) it be-

comes unnecessary to know the statistical sums A_1 and A_2 if these do not vary with temperature.

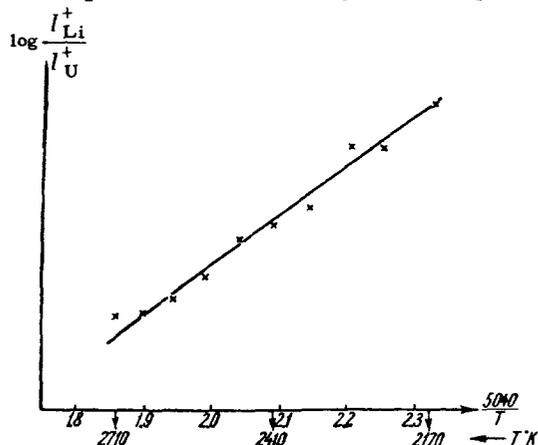


FIG. 13. Graph for determining the ionization potential of uranium⁷⁷ by comparing the positive surface ionization of two elements.

PSI with the production of alkali metal ions has been observed in the ionization of KCN , KCNS ,⁷⁸ and Na_2S ⁷⁹ molecules on tungsten.

In conclusion it should be noted that PSI involving a considerable number of additional elements

and surfaces could be investigated by using the mass-spectrometric technique and secondary ion and electron multipliers to record ion currents.

12. Investigation of Positive Ion Energy Distribution

A direct and independent proof of the hypothesis of thermodynamic equilibrium between a metal and adsorbed atoms, which is a basis for all emission equations, can be provided by investigating the energy distribution of particles leaving the surface. This was done by Ionov, using a retarding field,⁸⁰ for potassium ions produced in the PSI of potassium atoms and its halides on tungsten.

The molecular beam method was used. An intermediate cylindrical electrode with a ring-shaped slot, placed between the filament and measuring cylinder, was at a constant potential with respect to the filament, thus accelerating either positive ions or electrons. A smoothly regulated potential difference was applied between the filament and collector to retard ions or electrons. Figure 14

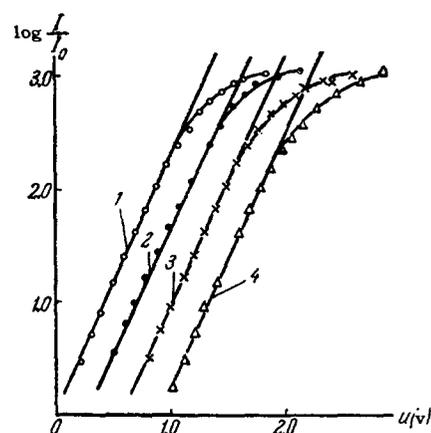


FIG. 14. Retardation curves for K^+ ions in surface ionization on W. 1—K atoms, 2—KBr molecules, 3—KCl molecules, 4—Thermoelectrons. $T = 2050^\circ\text{K}$.⁸⁰

shows the retardation curves for K^+ ions in the ionization of K, KBr and KCl and for thermoelectrons from the same filament at $T = 2050^\circ\text{K}$. The temperature was measured by means of the filament current with evidently low accuracy, as already noted. The straight-line segments of the ion and electron retardation curves in Figure 14 are seen to have very similar slopes, thus suggesting that the ion and thermoelectron distributions represent the same temperature. This temperature agrees with the filament temperature within the broad limits of accuracy of the measurements. These results provide an experimental proof that in SI on tungsten thermal equilibrium is established between the surface and adsorbed atoms and that, consequently, the accommodation

coefficient of the particles is close to unity.

A similar investigation in the case of SI on platinum would be of interest in connection with Sec. 10.

13. Positive Surface Ionization in Electric Fields

When PSI is being investigated on patchy surfaces in electric fields it must be remembered that experimental results can be compared with the theory only in the range of fields corresponding to the normal Schottky effect. In weak fields the contact field of the patches increases the heat of evaporation of ions from patches with the highest values of φ_k , but this fact cannot be taken into account analytically as the structure of the patchy surface is unknown. The anomalous Schottky effect for polycrystalline tungsten may include fields up to $\sim 10^4$ v/cm.

The growth of the ion current with the field has been noted in all papers on PSI, but the results were at first treated differently. Morgulis²³ observed the linearity of $\log I^+ = f(E)$ in the ionization of Na on W in fields up to 1.5×10^4 v/cm, and attributed the growth of α with E to a shift of ϵEx_0 in the valence electron level of an adsorbed atom at distance x_0 from the metal surface. Dobretsov²⁴ has shown that we would then have to assume $x_0 \sim 10^{-6}$ cm, which is unlikely.

Unlike Morgulis, Dobretsov attributed the growth of the ion current with the field to a reduction of $\epsilon\sqrt{\epsilon E}$ in the heat of evaporation λ_+ of ions and to the resulting increased relative probability W_2 that adsorbed atoms would evaporate as ions [Eq. (8)].²⁴ It has been shown in Sec. 2 that different field ranges correspond to different laws for the variation of α . Figure 4 shows that in moderate fields ($10^4 < E < 10^6$ v/cm) the effect of the field practically amounts to only a reduction of λ_+ by $\epsilon\sqrt{\epsilon E}$. The Morgulis correction must be taken into account in stronger fields. The variation of the heats of evaporation λ_+ and λ_0 in inhomogeneous fields because of ionic and atomic polarizability may evidently be neglected in all fields up to 10^6 v/cm.

A considerable number of experiments performed with the aim of clarifying the relationship $\alpha = f(E)$ did not yield very definite results. Besides Morgulis, the linearity of $\log \alpha = f(E)$ was observed by Copley and Phipps¹² for the ionization of K on W in fields up to 1.5×10^4 v/cm, and by Romanov and Starodubtsev^{33, 34} for PSI of sodium and lithium on W in fields up to 5×10^4 v/cm. In Dobretsov's paper²⁴ on PSI of K and Na on W up to $E \sim 10^5$ v/cm and in Konozenko's paper³⁰ on PSI of Na on thoriated W up to $\sim 4 \times 10^4$ v/cm it is

asserted that $\log \alpha$ is proportional to \sqrt{E} ; this is unconvincing since the experimental values are not well fitted by straight lines representing $\log \alpha = c\sqrt{E}$. Reference 31 reports the observation of a very weak linear relationship $\log \alpha = f\sqrt{E}$ for the ionization of Na on W and Pt, and on W partially coated with Pt, in fields from 3×10^3 v/cm to 1.5×10^4 v/cm.

The fields used in all of these experiments were insufficient to obtain reliable results for the relationship $\alpha = f(E)$ which could be compared with the theory, since they did not extend far outside the region of the anomalous Schottky effect (all experiments used polycrystalline surfaces). Also, in most of the experiments secondary currents from the collector were inadequately inhibited. The experimental determination of the relationship $\alpha = f(E)$ therefore still remains to be achieved.

Zandberg^{53, 37} has investigated $\alpha = f(E)$ for the ionization of K atoms and KCl and CsCl molecules, as well as of NaCl and LiCl molecules on W, in fields up to $\sim 10^6$ v/cm. Zandberg and Ionov³⁸ investigated PSI of Li atoms on W in the same fields, the results of which may be treated without any hypothesis regarding the adsorption of chlorine atoms on W or the possibility of incomplete dissociation of the molecules. Since relatively large E was used for the first time in these investigations and the results are treated from the point of view of PSI on patchy surfaces, we shall give a somewhat more detailed discussion.

The experimental investigation of $\alpha = f(E)$ presents two cases, $V < \varphi + \psi$ and $V > \varphi + \psi$, which require different techniques. For E up to $\sim 10^6$ v/cm we may assume $\psi = \sqrt{\epsilon E}$. I^+ and β can always be determined experimentally. Since β and α are related by (3), when $V < \varphi + \sqrt{\epsilon E}$ and α is large the variation of α with E for each patch on the surface according to (13) does not appreciably affect I^+ or β . In this case the temperature threshold of ionization is sensitive to E. The shift of temperature thresholds in SI of KCl and CsCl molecules was first observed and explained by Ionov.⁶⁷

Zandberg⁵³ has measured the ionization curves $\frac{I^+}{I_m^+} = f(T)$, where I_m^+ is the current at the curve maximum, in the region of threshold T with E ranging from $\sim 3 \times 10^4$ v/cm to 2×10^6 v/cm. Figure 15 shows some typical examples of these curves, which establish the dependence of ionization threshold temperatures T_0 on E. It was found, in agreement with (36) that T_0 decreases linearly as \sqrt{E} increases (Fig. 16), thus confirming (14) for each patch of the surface as E varies

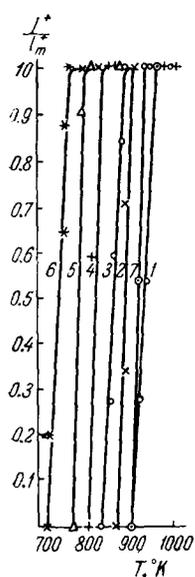


FIG. 15. Shift of threshold temperatures for the ionization of K on W in different fields from $E = 28.3$ kv/cm (1 and 7) to $E = 1981$ kv/cm (6).⁵³

from $\sim 10^4$ v/cm to 2×10^6 v/cm. Such fields actually affect α only by reducing the heat of evaporation of ions.

Had fields E_0 been reached in which $\sqrt{\epsilon E_0} = \frac{\epsilon}{4x_0}$, the threshold shift would have obeyed a different law with further increase of E ; up to $E = 2 \times 10^6$ v/cm this was not observed. The possible upper limit of x_0 for the ionization of K atoms and KCl and CsCl molecules on W can therefore be estimated. Assuming $E_0 \geq 2 \times 10^6$ v/cm, we obtain $x_0 = \frac{1}{4} \sqrt{\frac{\epsilon}{E}} \leq 6.7 \times 10^{-8}$ cm.

Ionov⁶⁷ measured T_0 in fields which were probably at least one order of magnitude higher. T_0 was practically reduced to room temperature; this evidently provides a basis for assuming that x_0 is close to the atomic or ionic radius.

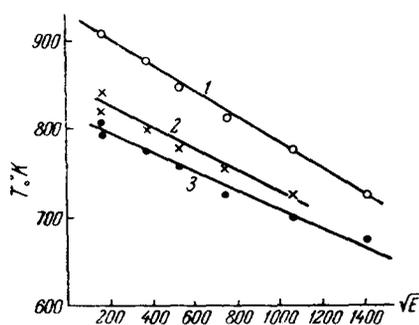


FIG. 16. Field dependence of ionization threshold temperature T_0 for ionization on W: 1 - K atoms, 2 - KCl molecules, 3 - CsCl molecules.⁵³

In reference 53 the temperature hysteresis of K-atom ionization on W was observed; this is very pronounced in weak fields. Slight temperature hysteresis in the ionization of Cs atoms on W and Re was also reported in references 42 and 55.

This effect, which is associated with the dependence of ionic heat of evaporation on the degree of surface covering by adsorbed atoms, has remained uninvestigated.

In the investigation of PSI of NaCl and LiCl molecules³⁷ and Li atoms³⁸ on W (with $\phi_{k \min} + \sqrt{\epsilon E} < V < \phi_{k \max} + \sqrt{\epsilon E}$) ion currents were measured at high tungsten temperatures ($T > 1800^\circ\text{K}$), when it could be assumed that the surface was not covered by adsorbed oxygen or chlorine. Under these conditions and with a large potential difference between the filament and measuring cylinder, currents of photoelectrons and secondary electrons ejected from the cylinder surface by ions are several times greater than the true ion currents of PSI and distort the relations $I^+ = f(T)$ and $I^+ = f(E)$. These secondary currents were effectively suppressed by introducing highly transparent ($\sim 98\%$) grids between the filament and measuring electrode, with potentials determined experimentally to keep the secondary currents below 5% of the measured PSI current.³⁷

Ion currents were measured in the collector circuit during PSI of NaCl and LiCl molecules and Li atoms as a function of filament temperature, in different fields ranging from 5.5×10^4 v/cm to 1.3×10^6 v/cm with constant molecular beam density; $\log I^+ = f\left(\frac{1}{T}\right)$ was thus obtained for different E . Figure 17 shows typical graphs of $\log I^+ = f\left(\frac{1}{T}\right)$ for the ionization of NaCl molecules on W. For LiCl

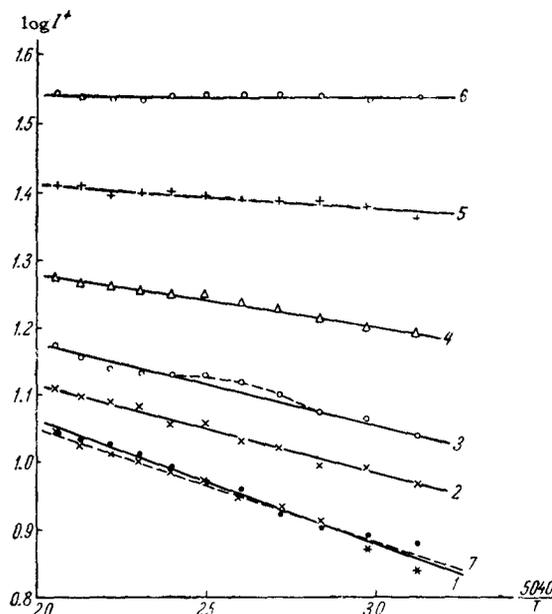


FIG. 17. $\log I^+ = f\left(\frac{1}{T}\right)$ for the ionization of NaCl molecules on W in different fields ranging from $E = 5.5 \times 10^4$ v/cm (1 and 7) to $E = 1.28 \times 10^6$ v/cm (6).³⁷

and Li as well as for NaCl these relations are represented with sufficient accuracy by straight lines with negative slopes which decrease as E increases. This suggests that in the given temperature range A^* is practically independent of T , so that (24) can be used, which gives the decrease of the line slope as E increases. The value of φ^* was estimated from the slope of $\log I^+ = f\left(\frac{1}{T}\right)$ according to (24). In the ionization of NaCl φ^* remains constant ~ 4.86 v up to 3.7×10^5 v/cm, but decreases in stronger fields to ~ 4.7 v at $E \cong 1.3 \times 10^6$ v/cm. For LiCl molecules and Li atoms in the same temperature range $\varphi^* \cong 5.1$ v, remaining constant up to $E = 7.3 \times 10^5$ v/cm; the decrease of φ^* begins in stronger fields for LiCl than for NaCl. The effective work function of W in the ionization of Li is thus higher than for Na, and in both cases exceeds φ_e^* . The decrease of φ^* in strong fields is associated with the rebalancing of terms in the sums of (23) and (33) owing to the increase of the term $\sqrt{\epsilon E}$, and naturally begins at lower E for Na than for Li, since $V_{Na} < V_{Li}$. The ionization of both Na and Li on W must be assigned to the general case c) considered in Sec. 4. The negative slopes of $\log I^+ = f\left(\frac{1}{T}\right)$ indicate that the first sum in (23) determines the temperature dependence of the current in SI of Na and Li on W .

The potential difference $(\varphi^* - \varphi_e^*)$ can be regarded as a measure of the average surface inhomogeneity. In the ionization of Li atoms on W this difference was determined directly by simultaneous measurements of the electron and ion currents from the filament. It follows from (27), (38) and (24) that

$$\log \frac{I^+ I_e}{T^2} = \log A^* B^* \epsilon + \frac{5040}{T} (\varphi^* - \varphi_e^* - V + 2\sqrt{\epsilon E}) \dots \quad (40)$$

With $\log I^+ = f\left(\frac{1}{T}\right)$ and $\log I_e = f\left(\frac{1}{T}\right)$ linear we may regard A^* and B^* as practically independent of T and determine $(\varphi^* - \varphi_e^*)$ from the slope of $\log \frac{I^+ I_e}{T^2} = f\left(\frac{1}{T}\right)$, a typical graph of which is shown in Figure

18. $(\varphi^* - \varphi_e^*)$ in different experiments with different filaments ranges from 0.5 to 0.8 v; this indicates that the patchy structure of the tungsten surface is not constant.

The fact that φ^* is independent of E for the ionization of LiCl and Li in all fields and for the ionization of NaCl in all fields except the strongest made it possible to check the relation $I^+ = f(E)$ expressed by (27), (28) and (33). Plots of $T \log I^+ = f(\sqrt{E})$ for different T (Fig. 19) are parallel

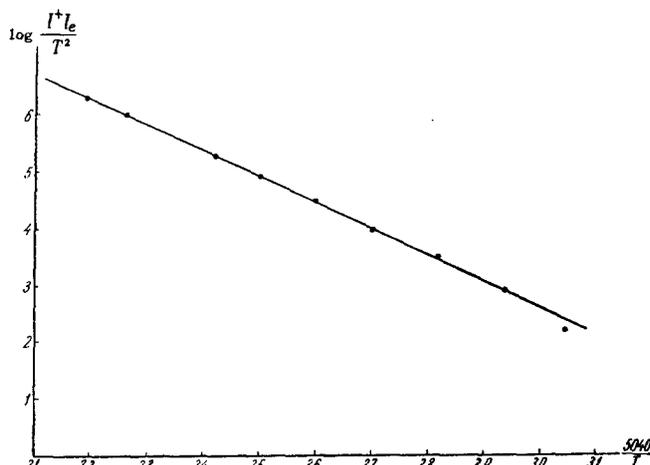


FIG. 18. Graph for determining $(\varphi^* - \varphi_e^*)$.³⁸

straight lines in agreement with (27), because A^* depends only slightly on T and E [Eq. (33)]. However, while for ionization on a homogeneous surface or on an inhomogeneous surface subject to the condition $\epsilon(V - \varphi_{k \max} - \psi) \gg kT$ the slopes

must have the constant value $\frac{\epsilon^{3/2}}{k} = 1.91$, in the general case the slope will be lower than $\frac{\epsilon^{3/2}}{k}$, as was shown in Sec. 4. It was found, indeed, that the slope of $T \log I^+ = f(\sqrt{E})$ for the ionization of NaCl molecules is lower than for LiCl; in the latter case the slope was in the range 1.6–1.8.

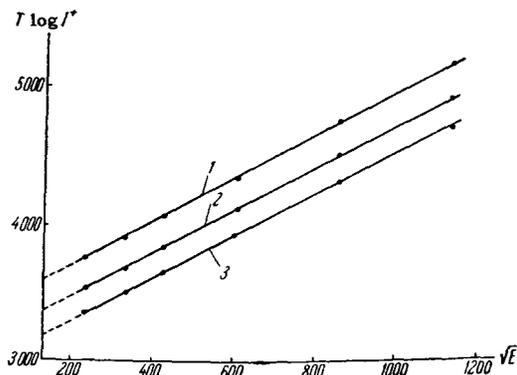


FIG. 19. $T \log I^+ = f(\sqrt{E})$ for the ionization of Li atoms on W :³⁸ 1) $T = 2460^\circ\text{K}$; 2) $T = 2340^\circ\text{K}$; 3) $T = 2240^\circ\text{K}$.

The investigation of PSI of Li atoms on W at low temperatures showed that the temperature threshold of Li ionization is practically unchanged as E increases up to 1.3×10^6 v/cm, thus differing from the ionization of K atoms and KCl and CsCl molecules on W . Since a shift of the threshold results from a change in the degree to which a surface is covered by adsorbed atoms as the field is varied, it is evident that the adsorbed atoms are mainly in the atomic state when Li is ionized on W .

14. Determination of Isothermal Heats of Evaporation of Ions and Atoms from a Surface

Isothermal heats of evaporation of ions l_+ and atoms l_0 from the surface of a heated metal can be determined by investigating unsteady surface ionization processes. Isothermal heats of evaporation of ions and atoms of the same element are related to the ionization potential of the atoms and the work function of the surface by the well-known Schottky equation $l_0 - l_+ = \epsilon(\varphi - V)$.⁸¹ The difference $l_0 - l_+$ can be obtained from this equation when φ and V are known, although the absolute values of l_0 and l_+ are of great interest for the study of adsorption effects.

Moon and Oliphant⁸² proposed a method for determining l_+ in cases when the adsorption of atoms on surfaces satisfies the relation $\varphi > V$; this procedure has been used a number of times.^{58,83,106} Evans determined the heat of evaporation of potassium, rubidium, and cesium ions from a polycrystalline tungsten surface. Arifov and Lovtsov⁸⁴ later made technical improvements in this procedure.

Starodubtsev⁸⁵ developed a method of determining l_0 and l_+ which is suitable in principle for any element that can ionize on a surface. We shall review briefly this method, used by Starodubtsev to measure the heats of evaporation of potassium and sodium on tungsten.

When a steady molecular beam impinges on a metal surface heated to the temperature T a very definite concentration N_1 of adsorbed atoms is established on the surface, corresponding to the steady ion current I_1^+ from the surface given by

$$I_1^+ = \epsilon N_1 \omega_+, \quad (41)$$

where $\omega_+ = Ce^{-l_+/kT}$ is the probability that adsorbed atoms evaporate as ions. If at some instant $t = 0$ access of atoms to the surface is interrupted (as by cutting off the molecular beam) the concentration of adsorbed atoms begins to diminish since the evaporation of adsorbed atoms as either atoms or ions will obey the law

$$\frac{dN}{dt} + a(T)N = 0, \quad (42)$$

where $a(T)$ is the probability of adsorbed atom evaporation, which for a small degree of surface covering by adsorbed atoms is represented by

$$a(T) = Ce^{-\frac{l_+}{kT}} + De^{-\frac{l_0}{kT}},$$

here C and D are slightly dependent on T . By means of the Schottky equation the last expression can be rewritten as

$$\begin{aligned} a(T) &= Ce^{-\frac{l_+}{kT}} \left[1 + \frac{1}{A} \exp \frac{\epsilon}{kT} (V - \varphi) \right] \\ &= De^{-\frac{l_0}{kT}} \left[1 + A \exp \frac{\epsilon}{kT} (\varphi - V) \right], \end{aligned} \quad (43)$$

where $A = \frac{C}{D}$ is the statistical sum ratio of ionic and atomic states of an adsorbed atom. The number of ions n_+ and of atoms n evaporating from the surface per second are given in the steady case by

$$n_+ = N_1 C e^{-\frac{l_+}{kT}}$$

and

$$n = N_1 D e^{-\frac{l_0}{kT}},$$

whence from (5) and the Schottky equation we obtain

$$a_0 = \frac{n_+}{n} = \frac{C}{D} \exp \frac{1}{kT} (l_0 - l_+) = A \exp \frac{\epsilon}{kT} (\varphi - V).$$

Equations (5) and (43) lead to

$$\left. \begin{aligned} Y_+ &= \ln \frac{a(T)}{1 + \frac{1}{A} \exp \frac{\epsilon}{kT} (V - \varphi)} = \ln C - \frac{l_+}{kT}, \\ Y_0 &= \ln \frac{a(T)}{1 + A \exp \frac{\epsilon}{kT} (\varphi - V)} = \ln D - \frac{l_0}{kT}. \end{aligned} \right\} \quad (44)$$

$Y_+ = f\left(\frac{1}{T}\right)$ and $Y_0 = f\left(\frac{1}{T}\right)$ must be straight lines whose slopes can be used to determine l_+ and l_0 . The plots require experimental determination of $a(T)$ for different T and of the denominators in the logarithms of (44). Starodubtsev has calculated the latter quantities for different T , assuming φ and V to be known, but assuming φ to be equal to φ_e^* although this, as we have seen, is impermissible for a complex surface. $a(T)$ is determined as follows. On the basis of (42) and (41) we can write

$$I^* = I_1^+ e^{-a(T)t}, \quad (45)$$

where I_1^+ is the steady ion current from the surface at temperature T and I^+ is the ion current at the time t after the beam is cut off. By interrupting the molecular beam periodically and observed the exponential current decay on the oscilloscope screen, $a(T)$ can be determined for any T and l_+ and l_0 can be determined by plotting (44).

The modulated molecular beam method used by Starodubtsev to determine $a(T)$ provides a sensitive means of influencing the state of the adsorbed atom layer both when $\varphi > V$ and $\varphi < V$. In the technique employed by Moon and Oliphant⁸² the adsorbed atom concentration is varied by suddenly reversing the potential difference between the filament and ion collector. But with $V > \varphi$, when the principal state of adsorbed atoms on the surface may be atomic, $a(T)$ cannot be determined by observing the time

variation of the current. Significant changes of the current in time can only occur if $V < \varphi$.

It must be emphasized that both procedures, that of Starodubtsev and that of Moon and Oliphant, can, strictly speaking, determine the heats of evaporation only in the case of homogeneous surfaces. Additional proof is required that they can be applied to complex surfaces. Indeed, besides the arbitrariness of φ in (44), the values of $a(T)$ are purely arbitrary for patchy surfaces. It follows from the Schottky equation $l_0 - l_+ = \epsilon(\varphi_K - V)$ for each patch of a complex surface that, in any case, the heat of evaporation difference $l_0 - l_+$ can vary widely on different portions of the surface.

15. Measurement of Ionization Coefficient β of Potassium Atoms on Tungsten

The technique for measuring heats of evaporation has been used by Arifov, Ayukhanov, and Lovtsov to determine the ionization coefficient of potassium atoms on tungsten.^{45,46} The advantage of this procedure for determining β lies in the fact that the need for determining n_0 is eliminated. As indicated in Sec. 6, n_0 is determined with low accuracy by any technique for supplying atoms to the surface.

When the potential difference between the collector and filament is reversed from positive to negative (the Moon and Oliphant technique)⁸² a burst of the ion current I_0^+ is observed, followed by its decay to a new value I_{∞}^+ (Fig. 20), resulting from the changed surface concentration of adsorbed atoms.

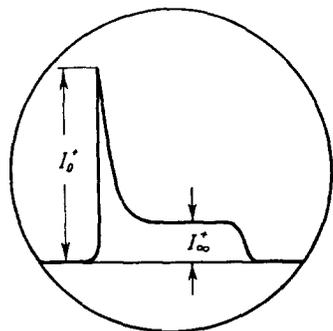


FIG. 20. Oscillogram of current from the surface ionization of K on W resulting from a square voltage pulse applied to the collector.⁴⁵

When the collector is positive we have

$$n_0 = N_1 D e^{-\frac{l_0}{kT}},$$

and when the collector is negative we have

$$n_0 = N_2 \left(C e^{-\frac{l_+}{kT}} + D e^{-\frac{l_0}{kT}} \right),$$

where N_1 and N_2 are the equilibrium concentrations of adsorbed atoms; therefore

$$\frac{N_1}{N_2} = 1 + \frac{C}{D} \exp \frac{1}{kT} (l_0 - l_+) = 1 + \alpha_0 \quad (46)$$

On the other hand, since $I_0 = \epsilon N_1 F C e^{-\frac{l_+}{kT}}$ and

$I_{\infty} = \epsilon N_2 F C e^{-\frac{l_+}{kT}}$, it follows that

$$\frac{N_1}{N_2} = \frac{I_0^+}{I_{\infty}^+}. \quad (47)$$

Equations (46), (47) and (3) lead to

$$\beta = \frac{I_0^+ - I_{\infty}^+}{I_0^+}. \quad (48)$$

Square voltage pulses were applied to the collector and I_0^+ and I_{∞}^+ were observed on the oscilloscope at different filament temperatures. The plot of $\beta(T)$, which was free of errors in determining n_0 , disagreed with (5), as was to be expected because the latter equation could not be applied to polycrystalline surfaces.

III. SURFACE IONIZATION WITH THE FORMATION OF NEGATIVE IONS (NSI)

It is now known that a large number of atoms, molecules and radicals can form stable negative ions in the gaseous phase.⁸⁶ Many of these can also be produced under suitable conditions through surface ionization on heated metals. We shall consider NSI with the formation of mainly atomic negative ions.

16. Negative Surface Ionization on Homogeneous Surfaces

When an atom that possesses electron-affinity levels is adsorbed on a surface, its evaporation from the surface can be described as in the first part of this article. The energy levels of the metal and the electron affinity levels of the adsorbed atom form a single system. A probability exists that an adsorbed atom evaporating from the surface will become a negative ion when $x \geq x_0$. The thermodynamic and statistical derivations of the degree of NSI are both formally analogous to the case of PSI. Since the reaction producing negative ions on a surface is the inverse of that producing positive ions (an electron is captured from the metal by an adsorbed atom in the first instance while an electron is transferred to the metal in the second instance), the expression for α in NSI on a homogeneous surface is derived from (5) by replacing φ with S and V with φ , as follows:

$$\alpha_0 = A_- \exp \frac{\epsilon}{kT} (S - \varphi), \quad (49)$$

where $A_- = \frac{Q_-}{Q_0}$ is the statistical sum ratio of the negative ion and atom.

The statistical derivation of the expression for α amounts to the determination of the probabilities W_1 and W_2 in (8). For NSI

$$W_1 = A_- \exp \frac{\epsilon}{kT} [S(x_0) - \varphi] \text{ and } W_2 = \exp \frac{\lambda'_0 - \lambda'_-}{kT}, \quad (50)$$

where $S(x_0)$ is the electron-affinity level of an adsorbed atom at the distance x_0 from the metal surface, and λ'_- is the energy expended in removing the negative ion from the surface.

We consider the following cycle: A negative ion X^- is carried from x_0 to $x = \infty$; an electron is removed from X^- ; the atom X is returned to x_0 , where it recombines with an electron. We thus obtain

$$\epsilon S(x_0) = \epsilon S + \lambda_- - \lambda_0. \quad (51)$$

It follows from (8), (50) and (51) that

$$\alpha = A_- \exp \frac{1}{kT} [\epsilon(S - \varphi) + (\lambda'_0 - \lambda_0) - (\lambda'_- - \lambda_-)]. \quad (52)$$

In zero external field E we have $\lambda'_0 = \lambda_0$, $\lambda'_- = \lambda_-$, and (52) becomes (49). When the external field E accelerating negative ions is not zero, we must, just as in the case of PSI, take into account: 1) the shift of the level $S(x_0)$, 2) the reduction of λ_- by $\epsilon\sqrt{\epsilon E}$, and 3) the variation of the heats of evaporation λ_0 and λ_- in an inhomogeneous field E .

Then

$$\alpha = A_- \exp \frac{\epsilon}{kT} \left[S - \varphi + Ex_0 + \sqrt{\epsilon E} + \frac{E^2}{2\epsilon}(a_0 - a_-) \right]. \quad (53)$$

Here a_- is the polarizability of a negative ion in an electric field E . In fields up to $10^6 - 10^7$ v/cm the terms Ex_0 and $\frac{E^2}{2\epsilon}(a_0 - a_-)$ can be neglected compared with $\sqrt{\epsilon E}$. In practice it is hardly possible to observe NSI in stronger fields because of field emission from the surface. Therefore

$$\alpha = A_- \exp \frac{\epsilon}{kT} (S - \varphi + \sqrt{\epsilon E}). \quad (54)$$

The negative ion current I^- is analogous to (20):

$$I^- = \frac{\epsilon n_0 F A_-}{A_- + \exp \frac{\epsilon}{kT} (\varphi - S - \sqrt{\epsilon E})}. \quad (55)$$

When the condition $\epsilon(\varphi - S - \sqrt{\epsilon E}) \gg kT$ is satisfied, (55) is simplified as follows:

$$I^- \cong \epsilon n_0 F A_- \exp \frac{\epsilon}{kT} (S + \sqrt{\epsilon E} - \varphi). \quad (56)$$

17. Negative Surface Ionization on Patchy Surfaces

Zemel³⁶ has derived an expression for the density of NSI on patchy surfaces without taking electric fields into account. In the general case of NSI on a patchy surface in a field that is sufficient to compensate the contact field of the patches the negative ion current from the surface is analogous to (22):

$$I^- = \epsilon n_0 A_- \sum_k \frac{F_k}{A_- + \exp \frac{\epsilon}{kT} (\varphi_k - S - \sqrt{\epsilon E})}. \quad (57)$$

When the condition

$$\epsilon(\varphi_{k \min} - S - \sqrt{\epsilon E}) \gg kT, \quad (58)$$

is satisfied, A_- in all denominators of the sum in (57) can be neglected compared with the exponential terms. Then

$$I^- = \epsilon n_0 A_- \exp \frac{\epsilon}{kT} (S + \sqrt{\epsilon E}) \sum_k F_k \exp \left(-\frac{\epsilon \varphi_k}{kT} \right). \quad (59)$$

(59) can be given a form similar to (24) as follows:

$$I^- = \epsilon n_0 A_-^* \exp \frac{\epsilon}{kT} (S + \sqrt{\epsilon E} - \varphi_-^*), \quad (60)$$

where

$$A_-^* = A_- \sum_k F_k \exp \frac{\epsilon}{kT} (\varphi_-^* - \varphi_k). \quad (61)$$

Here φ_-^* is the work function of the patchy surface averaged according to the negative ion current. φ_-^* is close in value to φ_e^* , since both thermoelectronic emission and negative ion emission are highest from spots with $\varphi_{k \min}$. However, $\varphi_-^* = \varphi_e^*$ only if the thermoelectronic constants B_k are identical for all patches.

18. Methodological Remarks

Most of our comments in connection with the study of PSI also apply to NSI. However, the technique for studying NSI must also make it possible to separate the negative ion current from the thermoelectron current, which at high temperatures exceeds the former by several orders of magnitude. Sutton and Mayer⁴ used a magnetron-type device to measure I^- and I_e separately. A magnetic field parallel to the cathode was generated by a solenoid. A specially designed grid, placed coaxially between the cathode and cylindrical anode, provided for complete separation of electron and ion currents. With the magnetic field switched on the electron current in the anode circuit, while vapor of the test element was absent, was reduced by a factor of $\sim 10^6$. I^- was measured by filling the magnetron with the given gas and switching on the magnetic field H . When H was switched off I_e was measured under the same conditions.

Glockler and Calvin⁸⁷ determined I_e and I^- by comparing the current-voltage characteristic of an ordinary diode filled with halogen vapor and the corresponding characteristic in a vacuum. By using the "3/2 law" for space charge they determined the effective carrier mass in the halogen vapor, from which they calculated the ratio $\frac{I_e}{I^-}$; this method is very inaccurate.

In the experiments of Dukel'skii and Ionov^{90,91} a cylindrical lens focused a ribbon-like beam of electrons and negative ions on the entrance slit of the ion collector. A magnetic field perpendicular to the beam deflected electrons to the anode, so that only negative ions from the cathode were registered in the collector circuit.

The most highly perfected procedure for studying NSI employs a mass-spectrometric technique which completely separates ion and electron currents and also separates the negative ion current of a given element from the current of impurity ions.

Beginning in 1935 many workers have studied NSI of halogens,^{4,87-93,97,98,113} oxygen,^{94,95} sulfur,⁷⁹ selenium and tellurium,¹⁰² and the radicals CN and CNS⁷⁸ on polycrystalline tungsten; of halogens on thoriated tungsten,^{99,101} and of antimony and arsenic on a thorium-oxide cathode.¹⁰² Quantitative results were obtained only for the halogens, oxygen, sulfur and CN on polycrystalline tungsten. In most of the experiments NSI was used as a method for determining the electron affinity of the atoms.

19. Measurements of the Temperature Dependence of the Negative Ion Current

The emission of thermoelectrons from a homogeneous surface is represented by the Richardson-Dushman equation

$$I_e = BFT^2 \exp \frac{z}{kT} (\sqrt{\varepsilon E} - \varphi). \quad (62)$$

Therefore when (58) is satisfied we have on the homogeneous surface, according to (56) and (62),

$$\frac{I_e}{T^2 I^-} = \frac{B}{\varepsilon n_{0,A-}} \exp \left(\frac{-\varepsilon S}{kT} \right), \quad (63)$$

and the current ratio $\frac{I_e}{I^-}$ is independent of φ and E even if φ depends on T .

When (58) is satisfied on an inhomogeneous surface, (37) and (59) lead to

$$\frac{I_e}{T^2 I^-} = \frac{C^*}{\varepsilon n_{0,A-}} \exp \left(-\frac{zS}{kT} \right), \quad (64)$$

where

$$C^* = \frac{\sum_k B_k F_k \exp \left(-\frac{z\varphi_k}{kT} \right)}{\sum_k F_k \exp \left(-\frac{z\varphi_k}{kT} \right)}. \quad (65)$$

It follows from (65) that C^* is slightly dependent on T ; we may therefore expect that in narrow temperature intervals (63) and (64) will be almost identical in representing the temperature dependence of

dence of $\frac{I_e}{T^2 I^-}$. If the thermionic constants B_k of all patches are identical, (63) becomes valid for a patchy surface for all values of E .

The temperature dependence of $\frac{I_e}{T^2 I^-}$ was verified by measuring NSI of iodine vapor on polycrystalline tungsten in a magnetron.⁹² In Fig. 21 the results are shown to agree with (63) and (64).

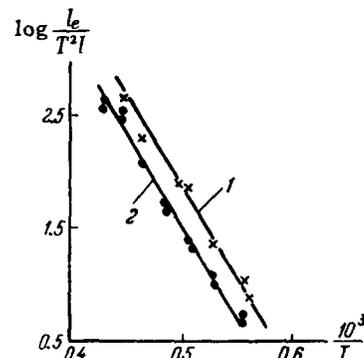


FIG. 21. Temperature dependence of $\log \frac{I_e}{T^2 I^-}$ for the emission of electrons and negative ions from a tungsten filament in iodine vapor.⁹² 1) $p = 0.3 \times 10^{-2}$ mm Hg; 2) 10^{-2} mm Hg.

In reference 60 $\log I^- = f\left(\frac{1}{T}\right)$ was checked for currents of the negative ions F^- , Cl^- , Br^- , and I^- produced in the surface ionization of NaCl, RbCl, CsCl, KBr, KI, and WCl_6 on W. The measurements were performed with a 180-degree magnetic mass spectrometer; beam strength constancy was controlled by measuring the current of positive alkali metal ions. In NSI of the given compounds only atomic negative ions of the halogens are formed. The negative ion spectrum always contained fairly strong peaks of ions with masses 24 and 26, which resulted from the ionization of organic vapors.

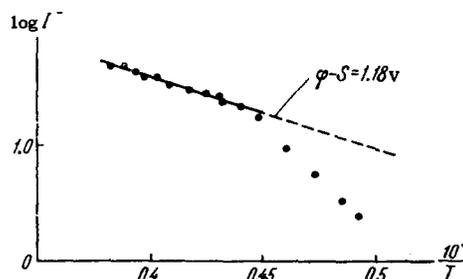


FIG. 22. Temperature dependence of negative Br ion current from the ionization of KBr molecules on W.⁶⁰

Figure 22 represents $\log I^- = f\left(\frac{1}{T}\right)$ for the current of negative Br^- ions resulting from SI of KBr molecules. Similar graphs were obtained by ionizing other salts. It is evident that $\log I^- = f\left(\frac{1}{T}\right)$ agreed with (56) or (60) only for $T > 2300^\circ K$, and that the slope of this graph gave a value of $(\varphi^* - S)$

(neglecting the correction $\sqrt{\epsilon E}$, which was ~ 0.02 v) that agreed with the difference between the values taken for ϕ_e^* and S . At $T < 2300^\circ\text{K}$ the tungsten surface was contaminated by electronegative gases, probably oxygen and the halogen; the work function then grew as well as the slope of $\log I^- = f\left(\frac{1}{T}\right)$.

Interesting results were obtained in NSI of ThCl_4 on W.⁶⁰ We know that at high temperatures thorium chloride on W is reduced to metallic thorium and produces a continually renewed coating on W with a low work function. In NSI of ThCl_4 the negative ion spectrum reveals both Cl^- and Cl_2^- ions. Since the electron affinity of Cl_2 molecules is below that of Cl atoms, Cl_2^- ions could appear in appreciable numbers only through SI on a surface with low ϕ_e .

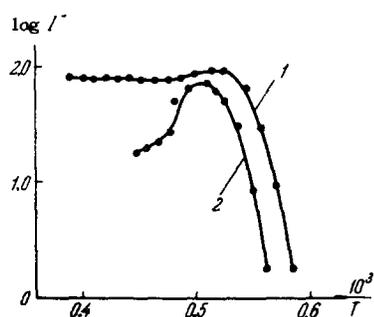


FIG. 23. Temperature dependence of negative ion current of Cl^- (1) and Cl_2^- (2) from the ionization of ThCl_4 on W.⁶⁰ The Cl_2^- current has been multiplied by 20.

Figure 23 represents $\log I^- = f\left(\frac{1}{T}\right)$ for Cl^- and Cl_2^- ions. For $T > 1900^\circ\text{K}$ the Cl^- current remains approximately constant. The sharp drop of the Cl_2^- current for $T > 2000^\circ\text{K}$ evidently results from the thermal dissociation of Cl_2 molecules and Cl_2^- ions.

It appears from the foregoing results that the theoretical temperature dependence of I^- has been confirmed experimentally. This indicates that the possible formation of negative ions through the interaction of thermoelectrons with gas molecules in the enclosure does not play an important part in these experiments on NSI.

20. Determination of Electron Affinity by Means of Negative Surface Ionization

Equation (63) was used by Mayer and his co-workers to determine S for atoms of chlorine,^{89,97} bromine,⁹⁸ iodine,⁴ and oxygen.^{94,95} A magnetron was used to measure $\frac{I_e}{I^-}$; the cathode temperature T was obtained from the filament current. The number of halogen atoms was calculated from the measured molecular halogen pressure assuming complete molecular dissociation on the heated W surface. Values of S obtained in this manner are given in Table I (column 2); these are averages ob-

TABLE I

1	S(v)			
	2	3	4 ⁹¹	5 ⁶⁰
F	—	—	3.62 4.41	—
Cl	4.00 ⁸⁹ 3.72 ⁹⁷	—	3.71	3.70
Br	3.5 ⁹⁸	3.82 ⁸⁸	3.64	3.34
I	3.14 ⁴	3.24 ⁸⁷	3.31	3.42
O	3.1 ⁹⁴ 2.3 ⁹⁵	—	—	—

tained with many different values of $\frac{I_e}{I^-}$ at different temperatures and halogen pressures. The spread of S in different experiments amounts to a few tenths of a volt; this indicates a large error, in complete disagreement with the optimistic estimate of the authors.

The low accuracy of this method evidently results basically from the low accuracy with which $\frac{I_e}{I^-}$, n_0 and T are determined. The same investigators determined that volatile tantalum chlorides formed in the apparatus produced an additional current of chlorine-containing molecules to the cathode, which was not subject to control by a manometer and which in one instance⁸⁹ led to an excessive value of S for chlorine atoms.

Other possible sources of error are:

1. It was assumed without sufficient proof that the halogen molecules dissociated completely at all temperatures and that the accommodation coefficient of the molecules was 1.
2. The theoretical value of the thermionic constant B was used in Eq. (63), whereas its value could be different for a patchy surface [see (65)].
3. The experimentally measured current I^- was possibly too high because of impurity ions which could not be separated from the ion current under investigation. In experiments on NSI of oxygen^{94,95} the measured current I^- apparently consisted only of impurity ions. The most direct method of determining S —by the photo-ionization of negative ions—gave $S = 1.48$ v for oxygen atoms.⁹⁶ It would follow from (56) and (60) that with this value of S the current I^- would be too small to be measurable under the experimental conditions of references 94 and 95.

The foregoing comments also apply to the method for determining S which was used by Glockler and Calvin, whose results for Br^{88} and I^{87} are given in the third column of Table I.

In references 90 and 91 values of S for halides

were determined by measuring currents from SI of alkali halides on W. When MX molecules are ionized only atomic ions M^+ and X^- are formed. On the W surface the MX molecules dissociate into atoms which are partially ionized on evaporation. The formation of M^+ ions must obey (20) or (30), while that of X^- ions must obey (56) or (60) the value of n_0 is the same in both instances independently of the degree of molecular dissociation.

From (20) and (56) the current ratio for a homogeneous surface is

$$\frac{I^+}{I^-} = \frac{\left[1 + \frac{1}{A} \exp \frac{\epsilon}{kT} (V - \varphi - \sqrt{\epsilon E}) \right]^{-1}}{A_- \exp \frac{\epsilon}{kT} (S + \sqrt{\epsilon E} - \varphi)}. \quad (66)$$

For a patchy surface we have from (30) and (60)

$$\frac{I^+}{I^-} = \frac{F^* \left[1 + \frac{1}{A^*} \exp \frac{\epsilon}{kT} (V - \varphi^* - \sqrt{\epsilon E}) \right]^{-1}}{A^* \exp \frac{\epsilon}{kT} (S + \sqrt{\epsilon E} - \varphi^*)}. \quad (67)$$

In both (66) and (67) the numerator for the ionization of halides of K, Rb, and Cs is slightly dependent on T and is insensitive to small variations of φ or φ^* . Therefore replacement of φ in (66) or of φ^* in (67) by φ_e^* results in only a small systematic error in the ratio $\frac{I^+}{I^-}$. By measuring $\frac{I^+}{I^-}$ at different temperatures S can be calculated from (66) or (67). The advantage of this procedure lies in the fact that $\frac{I^+}{I^-}$ is independent of n_0 and of the degree of dissociation of MX molecules.

The requirement that the work function $\varphi_e^* \cong \varphi_-^*$ be determined independently is a disadvantage. In calculations using (66) the tabular value $\varphi_e^* = 4.52$ v was assumed. However, it is now well known that the work function of a real cathode may differ considerably from this value independently of the quality of tungsten and of its heat treatment.

It has also been noted that in experiments on SI of potassium fluoride the work function φ_e^* of tungsten rose as it adsorbed fluorine, which remained on the surface up to $T = 2600^\circ\text{K}$. Column 4 of Table I gives values of S measured in this manner for halogen atoms. Two values are given for F atoms, calculated for $\varphi_e^* = 4.5$ v and 4.9 v.

In these experiments the field E was sufficient to compensate the contact field of the patches; therefore it is more proper to use (67) than (66) for calculations. However, A_\pm in (67) depends on the structure of the patchy surface [(see (61))] and cannot be evaluated. This could be a source of the systematic error in the values obtained for S.

A mass-spectrometric technique⁶⁰ was subsequently used to determine S through the measurement of $\frac{I^+}{I^-}$ in the ionization of alkali halides. These values of S are given in column 5 of Table I.

In reference 78 an attempt was made to determine S for the radical CN by mass-spectrometric measurement of the current ratio $\frac{I^+}{I^-}$ of K^+ and CN^- in the ionization of KCN and KCNS on W. The values obtained for S were found to be temperature dependent. This indicates that in NSI with the formation of negative ions of the CN radical we may possibly have to take the excitation of its vibrational energy levels into account.

NSI can serve as a reliable means of determining the difference between the values of S for two elements.^{93,79,113} When beams of the molecules MX and MX_1 from two independent vaporizers impinge on the same surface the intensity ratio of the molecular beams equals the ratio of the currents of positive ions M^+ from the ionization of molecules in each beam, i.e., $\frac{n_0}{n_{01}} = \frac{I^+}{I_1^+}$. We can determine $S - S_1$

by measuring the current ratio of the negative ions X^- and X_1^- ; subject to the condition (58), from (59) we obtain

$$\frac{I^-}{I_1^-} = \frac{n_0 A_-}{n_{01} A_{-1}} \exp \frac{\epsilon}{kT} (S - S_1). \quad (68)$$

If n_0 and n_{01} remain constant during the measurements, $S - S_1$ can also be determined from the slope of $\log \frac{I^-}{I_1^-} = f \left(\frac{1}{T} \right)$. Such measurements for the atoms of all halogens are given in Table II. The differ-

TABLE II

$S_1 - S_2$	(v)
$S_{Cl} - S_{Br}$	0.21 ± 0.06
$S_{Cl} - S_I$	0.48 ± 0.03
$S_{Cl} - S_F$	0.21 ± 0.03
$S_{Br} - S_I$	0.27 ± 0.02
$S_{Br} - S_F$	0.03 ± 0.02
$S_F - S_I$	0.24 ± 0.04
$S_{Br} - S_S$	1.23 ± 0.05

ences $S - S_1$ for various pairs of halogens are seen to be in good agreement. Direct measurements reported in reference 93 show that S is lower for fluorine than for chlorine. The difference between the electron affinities of bromine and sulfur has been determined similarly.⁷⁹

It must be noted that NSI has been used to de-

termine S for only a small number of elements. However, as the mass-spectrometric technique becomes more sensitive it may be possible to measure S for many elements.

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