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Thermodynamic Analysis of Metal
Surfaces Covered by Electropositive Adsorbates

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1. Introduction

The purpose of this paper is to present a rigorous thermodynamic analysis of uniform metal surfaces covered by monolayers of adsorbed particles. The analysis applies to surfaces for which the work function of the substrate surface is larger than the electronegativity of the free atoms of the adsorbate. Such surfaces will be called underlined electropositive.

The first detailed experimental and theoretical study of electropositive surfaces has been performed by Langmuir and his co-workers [1] who investigated the emission properties of a cesiated tungsten surface. Subsequently, experimental and theoretical work has been presented by many authors. For thermionic conversion the most practical work is that of Rasor and Warner [2], and that of Gyftopoulos and Levine [3], [4].

The theories just cited have many common features. They also have, however, substantial differences. In all three theories it is assumed that a surface system can be identified and that electrons are transferred from the surface system to the surface of the substrate thus causing the

creation of electrostatic fields that in turn result in a reduction of the work function of the substrate. However, whereas Langmuir assumes that one electron per adsorbate particle is transferred to the substrate, both Rasor and Warner, and Gyftopoulos and Levine introduce in their respective theories the possibility that less than one electron per adsorbate particle is transferred on the average. This innovation, introduced in different forms in the two theories, provides one possible cause of the inconsistency observed by Langmuir at coverage greater than about 0.5 between the change in work function of the substrate calculated from electron emission data and that calculated from atom emission data.

Langmuir uses some thermodynamic relations supplemented by several correlations of his experimental results and derives the emission characteristics of the cesiated tungsten surface that he investigated. Rasor and Warner also use some thermodynamic relations supplemented by Langmuir's ion emission data and derive emission characteristics of cesiated refractory metal surfaces in general. Finally, Gyftopoulos and Levine adapt to surfaces empirical correlations that have been developed in the theory of molecular bonds, and combine these correlations with thermodynamic relations to derive emission characteristics for any electropositive surface.

For purposes of thermionic conversion and for degrees of coverage θ ($\theta = \sigma/\sigma_f$) greater than about 0.5 no satisfactory general theory exists at the present time. On the other hand, for degrees of coverage smaller than about 0.5, the range of operation of emitters in thermionic converters, a complete and rigorous thermodynamic analysis can be performed without use either of emission data or empirical correlations. The analysis is based on Langmuir's ideas. It is feasible because Langmuir showed experimentally that for θ smaller than about 0.5 the interparticle forces between cesium atoms adsorbed on tungsten are of the dipole-dipole type, and that the work function change caused by the adsorption can be fully accounted for by electrostatic effects only.

The analysis proceeds as follows. First, the thermodynamic potentials and random fluxes associated with a surface in mutual stable equilibrium with the adsorbate vapor are computed. Then the results are adapted to the problem of evaluation of the emission characteristics of the surface in a steady state.

2. Model for Surface in Thermodynamic Equilibrium

We will consider a piece of a refractory metal enclosed by a uniform electropositive surface of coverage θ in mutual stable equilibrium with the vapor of the adsorbate at temperature T and at pressure p^g. The vapor pressure of the substrate at T is usually much smaller than p^g and will be neglected.

For values of T and p^g of practical importance the vapor behaves as a mixture of perfect gases of electrons, singly-charged positive adsorbate ions, and neutral adsorbate atoms. All thermodynamic potentials and random fluxes of the vapor can be expressed as functions of p^g and T by means of the perfect gas relations.

The interfacial region may be represented by an electrically neutral surface system consisting of electrons and singly-charged positive ion cores of the adsorbate existing in the force fields of a structureless perfect conductor. The perfect conductor represents the bulk of the substrate and consists of electrons and ion cores of the substrate. The thermodynamic potential of each species of the surface system can be expressed as a function of T and the adsorbate density σ per unit substrate area (or the coverage θ) with the aid of a model for the interparticle forces. The density σ (or the coverage θ) as well as the random fluxes at the points just outside the surface can then be expressed as functions of p^g and T by means of the conditions for mutual stable equilibrium between surface and vapor, and for chemical equilibrium between species in the surface.

In the surface system, one effect of the force fields of the substrate is that each electron is strongly correlated with a singly-charged adsorbate positive ion core so that the pair may be regarded as an electrically neutral species. Each pair will be called an ionic particle. An approximate model for the ionic particles and their force fields may be based on the following assumptions: (1) The net effect of interactions between adsorbate and substrate is the formation of the ionic particles of the surface system; (2) Each ionic particle has two translational degrees of freedom along the surface and one vibrational degree of freedom normal to the surface; (3) The exchange plus correlation effects for electrons near the surface system are identical to the exchange plus correlation effects for electrons near the surface of the substrate in the absence of the adsorbate; (4) The electrostatic effects of the surface system are equal to the sum of the electrostatic effects of the ionic particles and of the surface of the substrate in the absence of the adsorbate; (5) For monovalent adsorbates, the ionic particle is defined as a neutral species A such that : (a) in the absence of interactions with other adsorbate particles, A has a permanent dipole moment M_o and a ground state energy ϵ_o; (b) A is polarizable and has a polarizability α; (c) interactions of A with other particles of its species are described by the dipole-dipole force law; and (d) the vibrations of A are represented by a one-dimensional harmonic oscillator with g_a-fold degenerate energy levels and a fundamental frequency ν. The values of M_o, ϵ_o, α, and ν are determined as follows.

The center of each adsorbate ion core is taken at a distance r_i from the surface of the perfect conductor equal to the ionic radius of the adsorbate. The ground state of each ionic particle is regarded as that state in which one valence electron of the adsorbate is distributed along the surface of the perfect conductor in accordance with the image-force law, and a singly-charged positive ion of the adsorbate is within a sphere of

radius r_i. Thus the dipole moment M_o including self-depolarization is given by

$$M_o = \frac{e\, r_i}{1 + [\alpha_i / 4\pi\epsilon_o\, (2\, r_i)^3]} = \frac{8}{9}\, e\, r_i \, ,\tag{1}$$

because the polarizability α_i of the positive ion core may be estimated by [3]

$$\alpha_i = 4\pi\,\epsilon_o\, r_i^3 \, .\tag{2}$$

By virtue of the image-force law the energy ϵ_o is found to be

$$\epsilon_o = \frac{e^2}{16\,\pi\,\epsilon_o\, r_i} + \overline{\epsilon}_{oi}\tag{3}$$

where $\overline{\epsilon}_{oi}$ is the energy of the internal structure of a free singly-charged positive ion. Finally, Luke [5] has shown that

$$\alpha = \frac{4}{3}\, \alpha_i \, .\tag{4}$$

The frequency ν may be estimated by assuming that the energy and amplitude of oscillation of the harmonic oscillator are respectively [4I] $-e^2/16\,\pi\,\epsilon_o\, r_i$ and r_i . It is given by

$$\nu = \frac{1}{2\,\pi\, r_i} \left(\frac{e^2/16\,\pi\,\epsilon_o\, r_i}{m_f} \right)^{1/2}\tag{5}$$

where m_f denotes the atomic mass of the adsorbate. In practical problems ν and T are such that

$$KT \gg h\nu \, .$$

3. Thermodynamic Potentials and Random Fluxes

The principal result sought in this study is the relation between the work function ϕ_e of the surface system and T, p^g, and other properties of the substrate. This result may be obtained in two steps. In the first step ϕ_e is expressed as a function of σ (or θ) and in the second σ is expressed as a function of T and p^g.

Assumptions 3 and 4 imply that ϕ_e is equal to the bare work function ϕ_{em} plus the electrostatic effects of the depolarized dipoles of the ionic

particles. With respect to the points just outside the surface the dipoles may be regarded as a continuous double layer [6]. It follows that

$$\Delta \phi \equiv \phi_{em} - \phi_e = \frac{e\, M_o\, \sigma/\epsilon_o}{1 + b\sigma}; \quad b = \frac{\alpha}{\epsilon_o\, r_i}, \tag{6}$$

where it has been assumed that the average depolarizing field is equal to $\Delta\phi/r_i$.

The condition for mutual stable equilibrium between the surface and the vapor requires that the potential μ_a^g of the neutral atoms in the vapor be equal to the potential μ_a^s of the ionic particles, namely

$$\mu_a^g = \mu_a^s. \tag{7}$$

This equation determines the dependence of σ on T and p^g.

The potential μ_a^g is given by the perfect gas relation

$$\mu_a^g = k\,T \ln \frac{p^g}{(kT)^{5/2}} \cdot \frac{h^3}{g_a\,(2\pi m_f)^{3/2}} + \bar{\epsilon}_{oa}, \tag{8}$$

where g_a and $\bar{\epsilon}_{oa}$ denote the degeneracy and energy of the internal structure of neutral adsorbate atoms.

By means of thermodynamic considerations it can be shown that $\mu_a^s(\theta, T)$ may be expressed as

$$\mu_a^s(\theta, T) = \mu_a^s(\theta^*, T) + \int_{\theta*}^{\theta} \frac{1}{\sigma_f\, \theta} \left(\frac{\partial \tau}{\partial \theta}\right)_T d\theta, \tag{9}$$

where $\mu_a^s(\theta^*, T)$ denotes the value of μ_a^s for an arbitrarily small degree of coverage θ^*, and τ the spreading force per unit length of the surface system. Use of the condition for chemical equilibrium between species in the surface yields that

$$\mu_a^s(\theta^*, T) = \left[\mu_{ci}^s(\theta^*, T)\right]_1 + \left[\mu_{ce}^s(\theta^*, T)\right]_1, \tag{10}$$

where $\left[\mu_{ci}^s(\theta^*, T)\right]_1$ and $\left[\mu_{ce}^s(\theta^*, T)\right]_1$ denote the <u>chemical potentials</u> at the points just outside the surface for ions and electrons, respectively. For θ^* very small, $\left[\mu_{ci}^s(\theta^*, T)\right]_1$ is given by the perfect two-dimensional gas relation

$$\left[\mu_{ci}^{s}(\theta^{*},\,T)\right]_{1} = kT\ln\frac{\nu\sigma_{f}\,\theta^{*}}{g_{i}}\cdot\frac{h^{3}}{2\pi m_{f}\,(kT)^{2}} - \frac{e^{2}}{16\pi\epsilon_{o}\,r_{i}} + \bar{\epsilon}_{oi}\,, \qquad (11)$$

and $\left[\mu_{ce}^{s}(\theta^{*},\,T)\right]_{1}$ is equal to the negative of the bare work function, namely

$$\left[\mu_{ce}^{s}(\theta^{*},\,T)\right]_{1} = -\phi_{em}\,, \qquad (12)$$

where g_{i} denotes the degeneracy of the internal structure of the adsorbate positive ions. The spreading force τ can be expressed as

$$\tau = \tau_{o} + \tau_{1}\,, \qquad (13)$$

where τ_{o} and τ_{1} denote the contributions to τ of very short range forces and very long range forces between ionic particles, respectively. Use of the van der Waals excluded area assumption yields that τ_{o} is given by

$$\tau_{o} = \frac{\sigma_{f}\,\theta kT}{1-\theta} = \frac{\sigma kT}{1-(\sigma/\sigma_{f})}\,. \qquad (14)$$

Two estimates of τ_{1} have been computed by Langmuir [7]. For relatively small values of θ an approximate expression τ_{1v} is found by means of the second virial coefficient:

$$\tau_{1v} = D_{v}\,T^{1/3}\,M^{4/3}\,\sigma^{2}, \qquad (15)$$

where

$$M = \frac{M_{o}}{1+b\sigma}\,, \quad \text{and} \quad D_{v} = 9.287\times10^{19}\,(ev\text{-}cm^{2/3})/coulomb^{4/3}\text{-}°K^{1/3}.$$

For values of θ approaching unity, an estimate τ_{1a} is obtained by assuming that the ionic particles are arranged on a hexagonal array on the surface of the substrate:

$$\tau_{1a} = D_{a}\,M^{2}\,\sigma^{5/2}, \qquad (16)$$

where $D_{a} = 7.52\times10^{31}\,(ev\text{-}cm)/coulomb^{2}$.

For the purposes of this paper it will be assumed that

$$\tau_{1} = (1-\theta)\,\tau_{1v} + \tau_{1a} \qquad (17)$$

for all values of θ.

Combination of Eqs. 7 through 17 yields the relation

$$A_a - \frac{B_a}{kT} = \ln \frac{p^g}{(2\pi m_f kT)^{1/2}} = \ln \Gamma_a , \tag{18}$$

where

$$A_a \equiv \ln \frac{\nu \sigma_f}{2 \exp(\alpha_m/k)} + \ln \frac{2\theta}{1-\theta} + \frac{\theta}{1-\theta} , \tag{19}$$

$$B_a \equiv \frac{e^2}{16\pi\epsilon_o r_i} + \phi_{em}^* - V_i - \Delta\mu , \tag{20}$$

$$\phi_{em} = \phi_{em}^* + \alpha_m T , \tag{21}$$

$$\Delta\mu = \frac{D_v M_o^{4/3} T^{1/3}}{b} \left\{ 3 - \frac{3+2b\sigma}{(1+b\sigma)^{4/3}} + \frac{1}{b\sigma_f} \left[4.5 - \frac{2+b\sigma}{(1+b\sigma)^{4/3}} - 2.5(1+b\sigma)^{2/3} \right] \right\} +$$
$$+ \frac{D_a M_o^2}{b^{3/2}} \left[\arctan(b\sigma)^{1/2} - \frac{(b\sigma)^{1/2}}{(1+b\sigma)^2} \right] , \tag{22}$$

Γ_a denotes the adsorbate neutral atom random flux density which is equal to the neutral atom emission rate density, ϕ_{em}^* the value of ϕ_{em} in the limit $T = 0°K$, α_m the temperature coefficient, and V_i the first ionization energy of adsorbate atoms ($V_i \equiv \tilde{\epsilon}_{Oa} - \tilde{\epsilon}_{Oi}$). Equation 18 relates σ or θ and, therefore, $\Delta\phi$ (Eq. 6) to T and p^g. It is expressed in terms of A_a and B_a because it can be shown that, in the limit $T = 0°K$, B_a is the enthalpy of desorption of neutral adsorbate atoms.

An alternative way of writing Eq. 18 is given by

$$kT \left(\frac{B_a}{kT} - \ln \frac{2\theta}{1-\theta} - \frac{\theta}{1-\theta} \right) = kT \ln \frac{\Gamma_{ao}}{\Gamma_a} , \tag{23}$$

where

$$\Gamma_{ao} = \frac{\nu r \sigma_f}{2 \exp(\alpha_m/k)} .$$

For electropositive surfaces of interest to thermionic conversion in the range of θ between 0.1 and 0.5 and a range of T of a few hundred degrees centered about some practical temperature, the ratio B_a/kT is much greater than unity whereas the quantity $\ln[2\theta/(1-\theta)] + \theta/(1-\theta)$ is of the

order of unity. In addition, the dependence of B_a on T is weak. It follows that the left-hand side of Eq. 23 may be regarded as a function of θ or σ only and, therefore, that θ or σ is approximately a function of $kT \ln (\Gamma_{ao}/\Gamma_a)$ only.

The electron random current density $(e\Gamma_e)_1$ at the points just outside is given by the Richardson equation. In addition, it can be shown that the adsorbate positive ion random flux density $(\Gamma_i)_1$ at the points just outside is given by

$$\ln (\Gamma_i)_1 = A_i - \frac{B_i}{kT} , \qquad (24)$$

where

$$A_i \equiv \ln \frac{\nu \sigma_f g_i}{2 g_a} + \ln \frac{2\theta}{1-\theta} + \frac{\theta}{1-\theta} \qquad (25)$$

$$B_i \equiv \frac{e^2}{16 \pi \epsilon_o r_i} + \Delta\phi - \Delta\mu . \qquad (26)$$

It can be easily verified that $(\Gamma_i)_1/\Gamma_a$ satisfies the Saha-Langmuir equation.

The preceding results can be represented in graphical forms. For example, graphs of $\Delta\phi$ vs. σ (Eq. 6) for Cs, K, Na, and Li on any uniform refractory metal surface are shown in Fig. 1. The only input information needed for each of these graphs is the ionic radius r_i of the adsorbate.

For each surface a graph of $\Delta\phi$ vs. θ can be made provided that the adsorbate density σ_f at a full monolayer is known in addition to r_i. The value of σ_f depends on the orientation of the surface of the substrate. For a cesiated tungsten surface graphs of $\Delta\phi$ vs. θ are shown in Fig. 2 for three values of σ_f.

Again for each surface and T a graph of B_a vs. θ (Eq. 20) can be made provided that the values of V_i and ϕ_{em}^* are specified in addition to those of r_i and σ_f. The value of the bare work function ϕ_{em}^* in the limit 0 °K depends on the orientation of the surface of the substrate. For a cesiated tungsten surface graphs of B_a vs. θ are shown in Fig. 3 for two values of T. It is seen from this figure that indeed the dependence of B_a on T is weak.

Finally, for each surface and each value of T a graph of either $\Delta\phi$ or ϕ_e vs. $kT \ln (\Gamma_{ao}/\Gamma_a)$ can be made by elimination of θ between Eqs. 6 and 23. Three such graphs are shown in Figs. 4 through 6. They correspond to cesiated surfaces with $\sigma_f = 3.56 \times 10^{14}$ cm^{-2}.

4. Comparisons with Experimental Data

Emission characteristics are measured under steady state conditions and not under conditions of thermodynamic equilibrium. Because of

mathematical difficulties steady state data obtained at temperature T
and coverage θ are analyzed by assuming that the work function ϕ_e, the
electron saturation current density J_s, the adsorbate positive ion current
density $\mathcal{J}_s$, and the adsorbate neutral atom emission rate density J_a^s have
the same values as the ϕ_e and corresponding random flux densities of the
surface at T and θ but in mutual stable equilibrium with the adsorbate
vapor.

Here θ is determined not only by p^g and T but also by the vapor tem-
perature T^g and the electric field conditions prevailing near the points just
outside the emitter.   It is such that the total emission rate of adsorbate
particles, ions plus neutrals, is equal to the total arrival rate. The prob-
lem has been discussed by Maugis [8]. For present purposes it is suf-
ficient to indicate the following.

Data reported vs. T and θ can be compared directly with corres-
ponding theoretical results.   For example, Langmuir and Taylor [1]
investigated a cesiated tungsten surface for which they report that:
$\phi_{em}^* = 4.76\ ev$; $\phi_{em} = 4.62\ ev$; $\alpha_m \simeq -2k$; $\sigma_f = 3.56 \times 10^{14}\ cm^{-2}$. Their
data on $\Delta\phi$ vs. θ and B_a vs. θ in the range T = 600 - 1000 °K are super-
imposed in Figs. 2 and 3 respectively. The agreement between theory
and experiment is satisfactory for values of θ up to about 0.5.

Data reported vs. vapor pressure p^g and vapor temperature T^g can
be compared with theory as follows.   For practical conditions of operation,
contributions of ion currents to the determination of the steady state value
of θ may be neglected.   The atom emission rate Γ_a (Eq. 18) is then taken
equal to the atom arrival rate $\Gamma_{\mu a}$ which in turn is assumed equal to the
atom random flux $p^g/(2\pi m_f kT^g)^{\frac{1}{2}}$ in the vapor.   Thus

$$A_a - \frac{B_a}{kT} = \ln \Gamma_{\mu a} = \ln \frac{p^g}{(2\pi m_f kT^g)^{\frac{1}{2}}}\ , \tag{27}$$

or equivalently

$$kT \left(\frac{B_a}{kT} - \ln \frac{2\theta}{1-\theta} - \frac{\theta}{1-\theta} \right) = kT \ln \frac{\Gamma_{ao}}{\Gamma_{\mu a}} \tag{28}$$

Equation 28 indicates that theoretical results on ϕ_e vs. $kT \ln (\Gamma_{ao}/\Gamma_a)$
can be directly compared with corresponding experimental data of ϕ_e vs.
$kT \ln (\Gamma_{ao}/\Gamma_{\mu a})$ taken over a limited range of T. Langmuir's data on $\Delta\phi$
are superimposed on Fig. 4, and data reported by Hatsopoulos and Rufeh [9]
on ϕ_e of a cesiated tungsten surface are superimposed on Fig. 5. The
data of Hatsopoulos and Rufeh correspond to: $\phi_{em} = 4.87\ ev$; $\alpha_m = 0$;
$\sigma_f = 3.56 \times 10^{14}\ cm^{-2}$; T = 1600 - 2000 °K. The agreement between theory
and experiment is satisfactory but limited to values of θ up to about 0.5.

The relatively small spread in $\Delta\phi$ or ϕ_e data plotted vs. $kT \ln(T_{ao}/T_{\mu a})$ is achieved only when the range of T is limited to few hundred degrees. Otherwise the spread can be larger as illustrated by the theoretical results shown in Fig. 7. These results are based on Langmuir's values given above.

5. Concluding Remarks

Attempts have been made to extend the preceding rigorous analysis to degrees of coverage greater than 0.5. A second species was introduced in the surface system with properties similar to those of the neutral species of Rasor and Warner [2]. In spite of many and extensive calculations, the results proved unsatisfactory when compared with emission data. The reason for the disagreement may be either that the force fields between particles were not adequately modelled, or that assumptions 1 through 5 of Sec. 2 are not valid for θ greater than 0.5, or both.

We conclude that no satisfactory general theory for electropositive surfaces exists in the range θ greater than 0.5.

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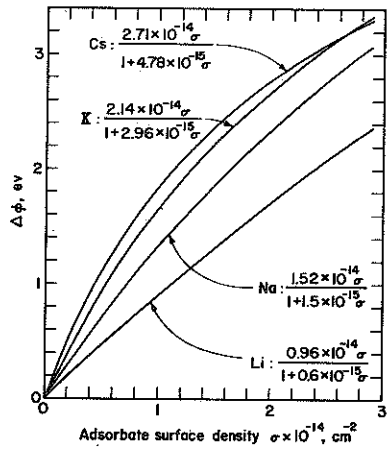[9] HATSOPOULOS, G. N., RUFEH, F., Thermodynamic correlation of work function, Energy Conversion, 10 (1970) 135.
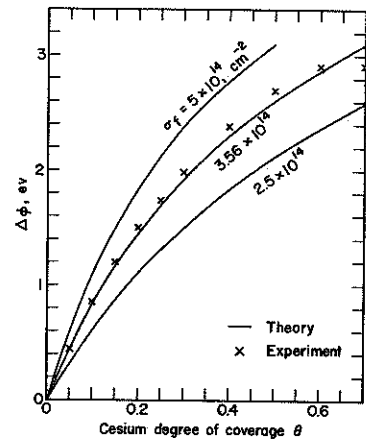
Fig. 1 Theoretical Results on $\Delta\phi$ vs. σ.

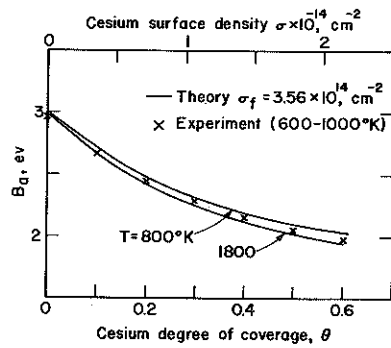Fig. 2 Theoretical and Experimental Results on $\Delta\phi$ vs. θ.

Fig. 3. Comparison of Theoretical and Experimental Values of B_a vs. θ.
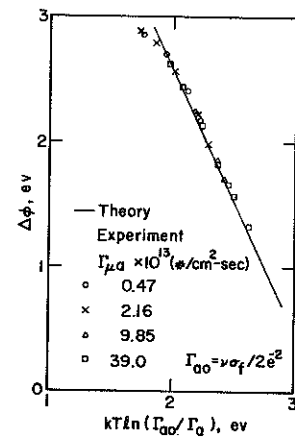

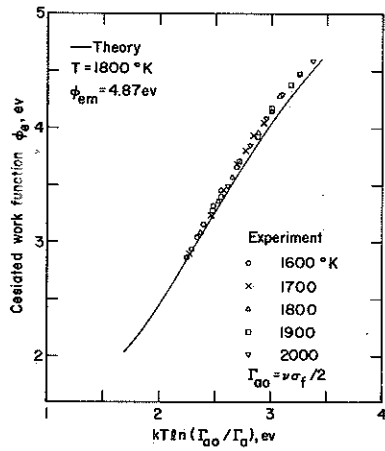Fig. 4 Comparison of Theoretical and Experimental Values of $\Delta\phi$ vs. $kT \ln (\Gamma_{ao}/\Gamma_a)$.

Fig. 5 Comparison of Theoretical and Experimental
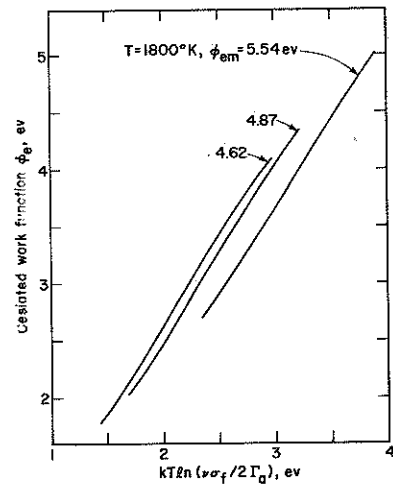Values of ϕ_e vs. $kT\ln(\Gamma_{ao}/\Gamma_a)$.

Fig. 6 Theoretical Graphs of ϕ_e vs. $kT\ln(\nu\sigma_f/2\Gamma_a)$ for
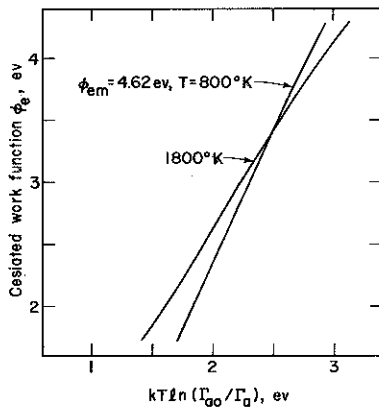Cesiated Surfaces ($\sigma_f = 3.56 \times 10^{14}$ cm^{-2}).

Fig. 7 Theoretical Results on ϕ_e vs. $kT\ln(\Gamma_{ao}/\Gamma_a)$
for T = 800 and 1800°K.