

ADSORPTION PHYSICS OF METALS PARTIALLY  
COATED BY METALLIC FILMS

Jules D. Levine and Elias P. Gyftopoulos

Department of Nuclear Engineering  
and  
Research Laboratory of Electronics  
Massachusetts Institute of Technology  
Cambridge, Massachusetts

Abstract: The physics of a metal partially covered by adsorbed metallic particles is successfully treated by using molecular physics and statistical mechanics. Theoretical equations are derived for desorption energies of atoms and ions, emission rates of atoms, ions, and electrons, and state functions relating the thermodynamic variables of the adsorption system. These equations are unique in the respect that they contain no adjustable constants. Comparison of theory with experiment is exceptionally good.

Introduction

The purpose of this paper is to present theoretical calculations of energies, rates, and equations of state for the particular adsorption system of metals partially covered by adsorbed metallic particles. Energies and rates of interest are the desorption energies of atoms and ions, and the emission rates of atoms, ions, and electrons. The equations of state, derived from simple rate balances, are useful because they relate the thermodynamic variables: surface coverage, surface temperature, vapor bath temperature, and electrostatic potential in the vicinity of the surface.

The paper includes only a brief outline of the important features of the theory and the main results. Detailed calculations, comparison with many experimental data and with other theoretical results will be presented in a future communication.

The analysis is unique in the sense that no adjustable constants are used; all calculations are expressed in terms of known or measurable physical constants.

The results of the study are important in general adsorption physics and are particularly applicable to thermionic energy converter technology.

## Desorption Energies of Atoms and Ions

Heats of desorption of atoms and ions are calculated by applying concepts of molecular physics to adsorption physics. The adsorbed particles are presumed to be of a single species and attached to the surface by partially ionic and partially covalent chemical bonds. The blended character of the bond is a direct extension from molecular physics, and it has already been successfully applied in calculating the electron work function of metals partially coated by metallic films. (1)

The heat of desorption  $\phi_a$  for an atom is taken as the sum of an ionic and a covalent contribution:

$$\phi_a = F\phi_e \left[ 1 + F(V_f - e^2/R)/\phi_e \right] + \sqrt{\phi'_m \phi'_f} S_{fm} \sqrt{1 - (F/v)^2} \quad (1)$$

ionic covalent

where  $\phi_e$  is the electron work function calculable as a function of coverage  $\theta$  (1),  $F$  is the fraction of charge transferred from the film to the metal, also calculable as a function of  $\theta$  from the dipole moment (1);  $R$  is the sum of the covalent radii of film and metal materials;  $S_{fm}$  is a calculable parameter containing the orbital strengths of the film and metal materials,  $\phi'_f$  and  $\phi'_m$  are the heats of sublimation of the pure film and metal materials respectively; and  $V_f$  and  $v$  are the ionization potential and the number of free valence electrons of the film atom, respectively.

The ionic contribution to the heat of desorption is obtained from a thought experiment in which a fractionally ionized (fraction  $F$ ) film particle is placed on the surface. For metallic particles adsorbed on transition metals numerical calculation shows that the ionic contribution is practically equal to  $F\phi_e$  for all values of coverage.

The covalent contribution is calculated by assuming that it is proportional to the orbital strengths and the amount of charge on the film and substrate particles. The constants of proportionality are chosen so that the covalent energy reduces to zero when the bond is purely ionic ( $F=v$ ) and to the heat of

sublimation of the bulk film material when the subscript indices are the same ( $m = f$ ). The geometric mean  $\sqrt{\phi_m \phi_f}$  is the direct analogue of Pauling's expression for the covalent energy of a diatomic molecule (2) and the orbital strength term  $S_{fm}$  appears in accordance with other findings of Pauling (3). A theoretical plot of  $\phi_a$  versus  $\theta$  for Cs on W is shown in Fig. 1. Superimposed are experimental data reported by Taylor and Langmuir (4) for the same surface. The agreement between theory and experiment is excellent, particularly since other workers (5) attempt to fit the same data with semi-empirical equations and adjustable parameters, but without success.

The heat of desorption  $\phi_p$  of an ion can be calculated in terms of  $\phi_a$ ,  $\phi_e$  and  $V_f$  by the energy balance

$$\phi_p = \phi_a - \phi_e + V_f. \quad (2)$$

Desorption heats for 13 films on W and for Cs on 21 transition metals have been calculated by means of Eqs. 1 and 2. Good agreement is established with the corresponding experimental data.

#### Desorption Rates of Atoms and Ions

The rates of atom desorption  $E_a$  and ion desorption  $E_p$  are calculated from a statistical mechanics formalism. In setting up the surface partition function, we presume that the film particles have two translational degrees of freedom parallel to the surface and one degree of vibrational freedom perpendicular to the surface. Under these conditions, and using the additional fact that there is no reflection of incident particles, the derived equations for  $E_a$  and  $E_p$  become

$$E_a = \left[ w_a \nu \sigma \theta e^{\Delta S/k} \right] e^{-\phi_a/kT} \quad (3)$$

and

$$E_p = \left[ w_p \nu \sigma \theta e^{\Delta S/k} \right] e^{-\phi_p/kT} \quad (4)$$

where  $w$  is the statistical weight,  $\nu$  is a calculable vibration frequency,  $\sigma$  is the surface density of adsorbed particles at one

monolayer,  $\theta$  is the coverage,  $\Delta S$  is a calculable quantity that may be interpreted as a configurational entropy difference, and  $T$  is the surface temperature.

The log of the bracketed term in Eq. 3

$$A_a = \log \left[ w_a v \sigma \theta e^{\Delta S/k} \right] \quad (5)$$

is computed as a function of  $\theta$  for Cs on W and is plotted in Fig. 2. Taylor-Langmuir<sup>(4)</sup> data of the same quantity are superimposed on the figure and compare very well with theory.

The same general statistical mechanics analysis can also be extended to calculate vaporization rates. This extension illuminates the correspondence between these processes, and is extremely useful in formulating the equations of state. The vaporization rate is given by the equation

$$E' = \left[ w_a' v' \sigma' \right] e^{-\phi'/kT'} \quad (6)$$

where  $w_a'$ ,  $v'$ ,  $\sigma'$  and  $\phi'$  are the direct analogues of the parameters in Eq. 3, and  $T'$  is the temperature of the vaporizing liquid. We easily show that the sublimation rate  $E''$  is given by an equation similar to Eq. 6.

Theoretically calculated vaporization and sublimation rates for bulk cesium are plotted in Fig. 3 where it can be seen that they correlate very well with experimental data. Similar results are obtained for other alkali metals.

#### Equations of State

Equations of state are calculated for the adsorption system in which a metal surface at temperature  $T$  is immersed in a vapor bath at temperature  $T'$ , and an electrostatic potential barrier  $\phi_x$  exists next to the surface. The general equation of state which relates the thermodynamic variables  $\theta$ ,  $T$ ,  $T'$ , and  $\phi_x$  is given by the rate balance

$$E_a + E_p e^{-\phi_x/kT} = E' \quad (7)$$

For various values of  $\phi_x$ , this general equation of state takes

on special forms that reveal some interesting characteristics of the adsorption system.

When  $\phi_x < 0$ , Becker<sup>(6)</sup> and others have shown that hysteresis effects arise when  $\theta$  or  $E_p$  is plotted versus  $T$  at a constant value of  $T'$ .

When  $\phi_x$  is allowed to vary in the range  $0 < \phi_x < \infty$ , different hysteresis effects appear when  $\theta$ ,  $E_p$ , or electron emission  $i_e$  are plotted versus  $\phi_x$  at constant values of  $T$  and  $T'$ . Some of these calculated effects are shown in Fig. 4. They appear only at low coverage and only over a narrow range of  $T$  and  $T'$ .

When  $\phi_x \gg kT$ , we have the very simple and useful equation of state

$$E_a = E' \quad (8)$$

which can be rearranged in the form

$$\frac{1000}{T} = \frac{\phi'}{\phi_a} \frac{1000}{T'} + \frac{\log\left(\frac{w_a \nu \sigma \theta e^{\Delta S/k}}{w_a \nu' \sigma'}\right)}{5.05 \phi_a} \quad (9)$$

If Eq. 9 is plotted on a graph with ordinate  $1000/T$  and abscissa  $1000/T'$ , the lines of constant  $\theta$  appear as straight lines whose slopes and intercepts can be calculated theoretically.

By combining this equation of state with the electron work function,  $\theta$  can be eliminated, and standard electron emission  $S$  curves can be constructed. One family of  $S$  curves is shown in Fig. 5 for Cs on a particular surface specified by the Taylor-Langmuir parameters  $\sigma = 4.8 \times 10^{14} \text{ cm}^{-2}$  and  $\phi_{em} = 4.62 \text{ ev}$ . Superimposed on the same figure are the data of Houston<sup>(7)</sup> and the extrapolated data of Taylor and Langmuir.<sup>(4)</sup> Agreement between theoretical and experimental  $S$  curves is exceptionally good. Similar results are obtained for Cs on other transition metals.

7. Houston, J.M., Thermionic Emission of Refractory Metals in Cesium Vapor, from Proceedings of the Round Table Discussion on Cathode Emission PIC-ELE-T1, 313, June 30, 1961, Power Information Center, Univ. of Penn.
8. Rasor, N.S. and C. Warner III, "Atomics International First Summary Report of Basic Research in Thermionic Energy Conversion Processes", p. 45, Nov. (1961).

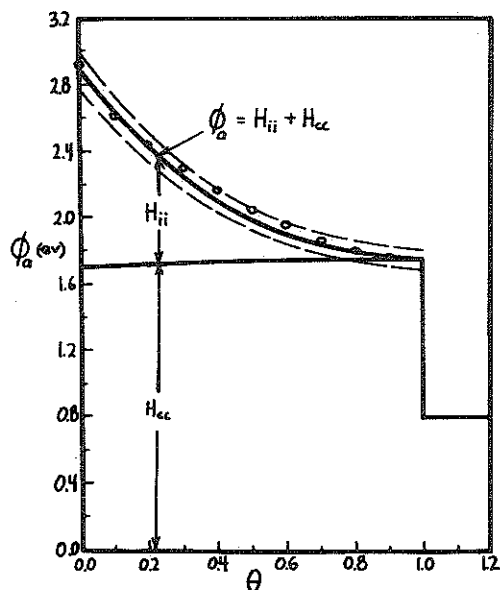


Fig. 1. Comparison of theoretical heat of atom desorption  $\phi_a$  for Cs on W (solid curve) with Taylor-Langmuir data<sup>a</sup> (circles).  $\theta$  is the film coverage expressed in monolayers. The 3% uncertainties inherent in  $\phi_a$  are shown by the dashed lines, and the ionic and covalent components  $H_{ii}$  and  $H_{cc}$  are also depicted.

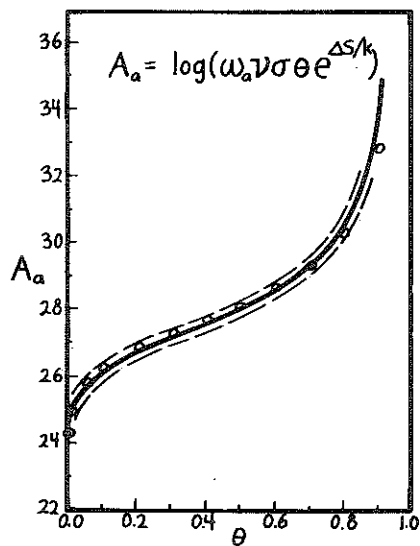


Fig. 2. Comparison of theoretical pre-exponential factor  $A_a$  for Cs on W (solid curve) with experimental Taylor-Langmuir values (circles). The uncertainties inherent in  $A_a$  are shown by the dashed lines.

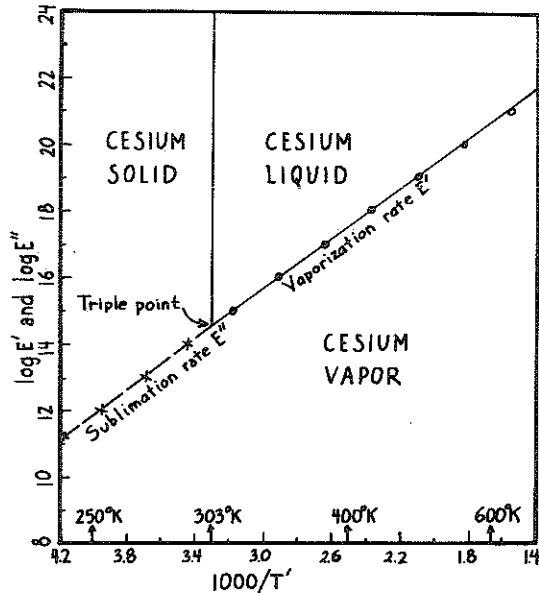


Fig. 3. Comparison of theoretical values of cesium vaporization rate  $E'$  and cesium sublimation rate  $E''$  (straight lines) with experimental values (circles and crosses). Note slight discontinuity in slopes at triple point.

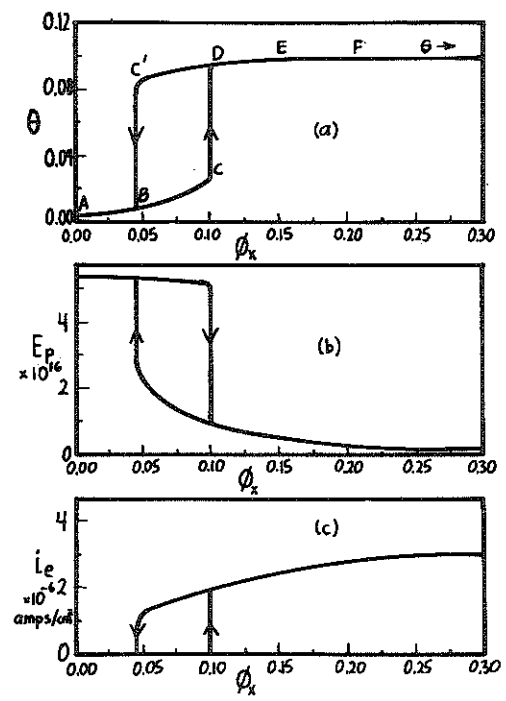


Fig. 4. Calculated hysteresis effects for Cs on W with  $T = 14000\text{K}$  and  $T' = 3660\text{K}$ . (a) Coverage versus external potential (volts), (b) ion emission versus external potential, and (c) electron emission versus external potential.



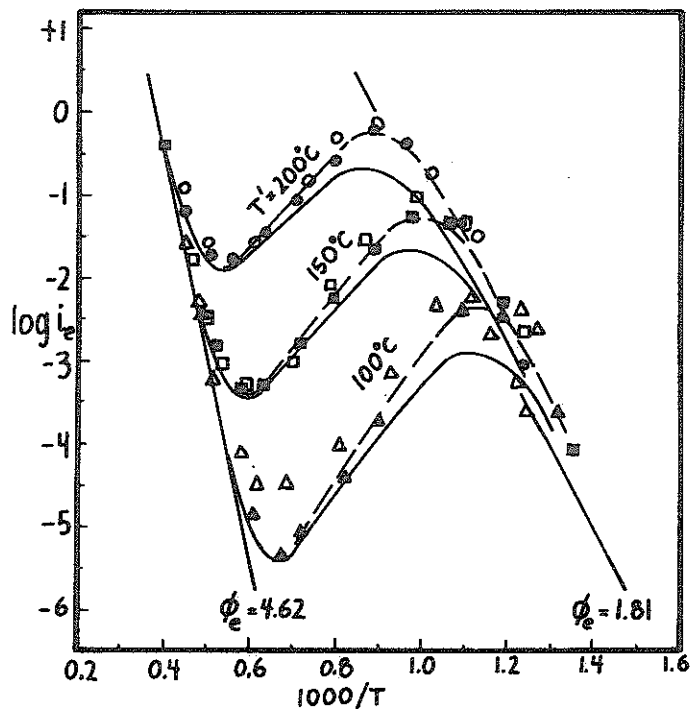


Fig. 5. Electron emission S curves for cesium adsorbed on tungsten. Calculated curves (solid lines) and "3% uncertainty curves" (dashed lines) for  $\phi_{em} = 4.62$  eV and  $\sigma = 4.8 \times 10^{14} \text{ cm}^{-2}$  are compared with extrapolated Taylor-Langmuir data (●, ■, ▲) and with Houston data (○, □, △).