

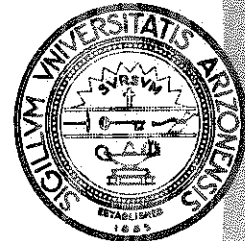
# A Symposium on

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CAMBRIDGE, MASS.

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Tucson, Arizona      February 19-21, 1964

WORK FUNCTION AND DESORPTION ENERGIES AND  
RATES OF REFRACTORY METALS COATED WITH CESIUM\*

by

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\*Presented at the Symposium on High Temperature Conversion of  
Heat to Electricity at the University of Arizona, Tucson,  
February 1964.

## INTRODUCTION

This paper is a summary of some work on the theoretical correlation of electron work function<sup>(1)</sup> and atom and ion desorption energies<sup>(2)</sup> and desorption rates<sup>(3)</sup> for metallic surfaces coated by monatomic metallic particles. The emphasis of the summary is on surfaces coated by cesium.

Reviews of the models and results of other workers are given in references (1-3) and they will not be repeated here.

The basis of the derived correlations is the assumption that, in the intermetallic adsorption systems of interest, the adsorbate particles are chemisorbed as a single species and that they are held onto the substrate by partially ionic and partially covalent bonds. The chemical nature of the surface bonds is suggested by their magnitude which is of the order of eV.

The surface is visualized as a composite "molecule". Thus, computational techniques developed for molecular physics are extended to adsorption systems. This procedure is suggested by the similarity of the physical interpretation of such quantities as ionization potential and electron work function, molecular dissociation energy and atom desorption energy etc.

## ELECTRON WORK FUNCTION

The electron work function of a composite surface is calculated through use of the concept of electronegativity. This is suggested both by the direct proportionality between the first ionization potential and the relative electronega-

tivity of an atom<sup>(4)</sup> and by the semi-empirical linear relationship between the work function,  $\phi_e$ , of a pure metallic surface and the relative electronegativity of the constituent element.<sup>(5)</sup> Specifically, in the latter case:

$$\phi_e = 2.27x + 0.34 \quad (1)$$

where  $x$  is the relative electronegativity.

Consider a homogeneous composite surface. This surface exhibits a relative electronegativity,  $x(\theta)$ , which determines an electronegativity barrier,  $e(\theta)$ , according to Eq. (1). This barrier would be identical with the work function if the individual molecules, made of substrate-adsorbate atoms, were not polarized. Since, however, the surface bonds are partially ionic and partially covalent, the surface molecules have a dipole moment which results in an electric double layer. The double layer determines a dipole barrier,  $d(\theta)$ , and thus the work function is

$$\phi_e = e(\theta) + d(\theta) . \quad (2)$$

The exact analytical representation of the electronegativity barrier is difficult to compute. It can be approximated, however, by a series expansion which satisfies the following boundary conditions. At  $\theta = 0$  the electronegativity barrier is that of the pure substrate and it is not substantially affected by the addition of a few adatoms.<sup>(6)</sup> Therefore

$$e(0) = \phi_m \quad ; \quad \left. \frac{de(\theta)}{d\theta} \right|_{\theta=0} = 0 \quad (3)$$

where  $\phi_m$  is the work function of the substrate. At one monolayer ( $\theta = 1$ ), it is experimentally observed that the work function reaches a constant value,  $\phi_f$ , characteristic of the adsorbate. This value does not change with the addition of more adatoms. Thus:

$$\phi(1) = \phi_f \quad ; \quad \left. \frac{d\phi(\theta)}{d\theta} \right|_{\theta=1} = 0 \quad (4)$$

The simplest polynomial expansion that satisfies Eqs. (3-4) is:

$$\phi(\theta) = \phi_f + (\phi_m - \phi_f)G(\theta) \quad (5)$$

$$G(\theta) = 1 - 3\theta^2 + 2\theta^3 \quad (6)$$

The dipole barrier can be derived from the electronegativity barrier. Indeed, a molecule consisting of two dissimilar atoms of relative electronegativities  $x_1$  and  $x_2$ , exhibits a dipole moment proportional to the difference of electronegativities,  $(x_1 - x_2)$ .<sup>(4)</sup> Assuming that this is also applicable to molecules formed between a site of a partially covered surface and an adatom, the surface dipole moment is:

$$M(\theta) = M_0(x(\theta) - x_f)/(x_m - x_f) = M_0G(\theta) \quad (7)$$

where  $M_0$  is the dipole moment of a single substrate-adsorbate molecule at zero coverage and  $x_m$ ,  $x_f$  the electronegativities of the substrate and the adsorbate atoms, respectively. Eq. (7) does not account for dipole-dipole interactions. If these are taken into consideration an effective dipole moment

results which is:<sup>(7)</sup>

$$M_e(\theta) = M(\theta)/(1 + 9\alpha\sigma_f^{3/2}\theta^{3/2}) \quad (8)$$

where  $\alpha$  is the polarizability of the substrate-adsorbate molecules and  $\sigma_f$  is the number of sites available for adatom occupancy per unit substrate area to form a monolayer. Thus, the dipole barrier is

$$d(\theta) = -4\pi\theta G(\theta)\sigma_f M_o / (1 + 9\alpha\sigma_f^{3/2}\theta^{3/2}) \quad (9)$$

The dipole moment at zero coverage is evaluated by assuming that the adatom is nested on four substrate atoms. Using the proportionality between dipole moment and electronegativity and accounting for self-depolarization<sup>(8)</sup> it is found that:

$$M_o = 4k(x_m - x_f)\cos\beta / (1 + \alpha/R^3) \quad (10)$$

$$\cos\beta = (1 - 1/2\sigma_m R^2)^{1/2} \quad (11)$$

where  $k$  is the constant of proportionality between dipole moment and difference of electronegativities ( $k = 1.15 \times 10^{-18}$  esu-cm),<sup>(4)</sup>  $\sigma_m$  the apparent surface density of the substrate and  $R$  the sum of the covalent radii of the substrate and the adsorbate.

Combination of Eqs. (2) through (10) yields:

$$\begin{aligned} \theta_m - \theta_e(\theta) / (\theta_m - \theta_f) &= \Delta\theta / (\theta_m - \theta_f) = \\ &= 1 - G(\theta) \left[ 1 - \frac{0.765 \times 10^{-14} \sigma_f \theta \cos\theta}{(1 + \alpha/R^3)(1 + 9\alpha\sigma_f^{3/2}\theta^{3/2})} \right] \end{aligned} \quad (12)$$

Note that the normalized variation of the work function is independent of electronegativities and any arbitrarily adjustable constants. It depends only on the lattice parameters of the substrate and the adsorbate. It is also worth noting that if  $\phi_e$  admits a minimum smaller than  $\phi_f$ , then there is a value of  $0 < \theta < 1$  for which  $\phi_e = \phi_f$ . This value of  $\theta$  is independent of  $G(\theta)$  and it suggests that the derived formula is relatively insensitive to the somewhat arbitrarily chosen expansion for  $e(\theta)$ .

Figure 1 is a comparison of Eq. (12) with reported experimental data for Cs on W.<sup>(9)</sup> Other implications of Eq. (12) are discussed in reference 1.

#### ATOM AND ION DESORPTION ENERGIES

The chemical nature of the surface bonds suggests that the atom desorption energy,  $\phi_a$ , can be written as:

$$\phi_a = H_{ii} + H_{cc} \quad (13)$$

where  $H_{ii}$  is the ionic and  $H_{cc}$  is the covalent contribution.<sup>(4)</sup>

The computation of the two contributions must be such that at least three conditions are satisfied. First,  $H_{ii}$  must vanish for purely covalent bonds. Second,  $H_{cc}$  must vanish for purely ionic bonds. Third, when material X is adsorbed on bulk material X,  $H_{cc}$  must reduce to the heat of sublimation of material X.

The ionic contribution  $H_{ii}$  is assumed to arise from a

fractional charge,  $F$ , of the adsorbate which is transferred to the substrate. The value of  $H_{11}$  is calculated through the following thought process. First, an adsorbed particle with a fractional charge  $F$  is removed to infinity. This requires an amount of energy  $F^2 e^2 / R$  where  $e$  is the electronic charge. Next, the fractional electronic charge  $F$  is removed from the surface to infinity. This requires an amount of energy  $F\phi_0$ . Finally, the two charges are combined to produce a neutral atom. This step requires an amount of energy  $F^2 V_f$ , where  $V_f$  is the ionization potential of the adsorbate. Summation of all the energies of the thought process yields:

$$H_{11} = F\phi_0(1 + \delta) \quad ; \quad \delta = F(e^2/R - V_f)/\phi_0 \quad (14)$$

Eq. (14) satisfies the stipulated requirement for  $F=0$ .

The fractional charge is related to the surface dipole moment but it is not uniquely definable because it is not possible to ascertain whether dipole-dipole interactions and/or self-depolarization correspond to charge transfer from the adsorbate to the substrate or not. Assuming that dipole-dipole interactions do not lead to charge transfer, it is found that

$$F = \frac{0.422(\phi_m - \phi_f)G(\theta)}{R(1 + \alpha/R^3)} \quad (15)$$

where  $\phi_m$  and  $\phi_f$  are in (ev) and  $R$  in Å.

The covalent contribution  $H_{cc}$  arises from pairing of valence charges. Thus, both the substrate and the adsorbate contribute to the bond. The contribution of the substrate is



taken proportional to the heat of sublimation,  $\beta_m^i$ , the square of the angular strength,  $S_m^2$ , (4,10) and the valence charge,  $q_m$ , of the substrate. In other words the contribution of the substrate is  $\sim \beta_m^i S_m^2 q_m$ . Similarly the contribution of the adsorbate is taken  $\sim \beta_f^i S_f^2 q_f$ . The simplest relationship that combines these two contributions and guarantees the necessary limiting requirements -  $H_{cc} = \beta_f^i$  for  $m=f$  and  $H_{cc} = 0$  for  $q_f = 0$  - is their normalized geometric mean:

$$H_{cc} = \left[ \beta_f^i \beta_m^i \cdot \frac{4S_f^2 S_m^2}{(S_f^2 + S_m^2)^2} \cdot \frac{4q_f q_m}{(q_f + q_m)^2} \right]^{1/2} \quad (16)$$

The valence charge dependence can be further simplified by the approximate relationships

$$q_f = v - F \quad ; \quad q_m = v + F \quad (17)$$

where  $v$  is the largest number of valence electrons participating in the covalent bond. Thus:

$$H_{cc} = (\beta_f^i \beta_m^i)^{1/2} S_{fm} Q_{fm} \quad (18)$$

$$S_{fm} = 2/(S_f/S_m + S_m/S_f) \quad ; \quad Q_{fm} = (1 - F^2/v^2)^{1/2} \quad (19)$$

The geometric mean of the heats of sublimation in Eq. (18) is analogous to the expression derived for molecular bonds. (4)

The factor  $S_{fm}$  can be interpreted as the angular efficiency and has been calculated for different adsorption systems in reference 2. The factor  $Q_{fm}$  can be interpreted as a charge efficiency.

The atom desorption energy is

$$\beta_a = F\beta_e(1 + \delta) + (\beta_f^i \beta_m^i)^{1/2} S_{fm} Q_{fm} \quad (20)$$

Note that it depends explicitly on physical properties of the

materials of the adsorption system and it does not involve any adjustable constants.

Figure 2 presents a comparison of theoretical and experimental results.<sup>(9)</sup> Other comparisons are given in reference 2.

The ion desorption energy,  $\beta_p$ , is readily calculated from the simple energy balance equation:

$$\beta_p = \beta_a + V_f - \beta_e \quad (21)$$

#### ATOM AND ION DESORPTION RATES

The atom and ion desorption rates are computed by means of statistical mechanics.<sup>(11)</sup> The adsorbed one species particles are assumed to have two degrees of translational freedom parallel to and one degree of vibrational freedom perpendicular to the surface. They are also assumed to be in equilibrium with the vapor phase. From the equality of the chemical potentials it is found that:

Atom desorption rate:  $E_a = \omega_a \sigma_f \nu \exp(\Delta S/k) \exp(-\beta_a/kT) \quad (22)$

Ion desorption rate:  $E_p = \omega_p \sigma_f \theta \exp(\Delta S/k) \exp(-\beta_p/kT) \quad (23)$

where  $\omega_i$  is the statistical weight of the  $i$ th species of vapor particles,  $\Delta S$  is the configuration entropy change given by

$$\Delta S = k \ln \left[ (A_t/A_f) \exp \theta \ln(A_t/A_f) / \partial \theta \right], \quad (24)$$

$T$  is the surface temperature,  $A_t$  is the total and  $A_f$  is the

free area for translation,  $\nu$  is the effective vibration frequency given by

$$\nu = \nu_1 \exp(\theta \partial \ln \nu_1 / \partial \theta) , \quad (25)$$

and  $\nu_1$  is the vibration frequency.

The free area is estimated through a combined consideration of the Van der Waals and the cage models:

$$A_f = A_t (1 - \theta)^{1/2} (1 - \theta^{1/2}) \quad (26)$$

This estimate fails for  $\theta \lesssim 1$  because then  $\Delta S \rightarrow \infty$ . The reason for this failure is that Eq. (24) does not account for the buildup of the second layer before the completion of the first. A discussion and computations on this subject are given in reference (3).

The vibration frequency  $\nu_1$  is derived by assuming that the surface molecules are harmonic oscillators.<sup>(12)</sup> The adsorbed particles of mass  $m_f$  are nested on four substrate particles each of mass  $m_m$ . The reduced mass of the oscillator is

$$\bar{m} = 4m_f m_m / (m_f + m_m) , \quad (27)$$

its energy is  $\phi_a$  and the amplitude of the oscillation is  $R \cos \beta$ . Thus:

$$\nu_1 = (1/2\pi R \cos \beta) \left[ \phi_a (m_f + 4m_m) / 2m_f m_m \right]^{1/2} \quad (28)$$

The desorption rates can also be written in the form

$$\log E_a = A_a - 5050 \phi_a / T ; A_a = \log \left[ \sigma_a \sigma_f \theta \nu \exp(\Delta S/k) \right] \quad (29)$$

$$\log E_p = A_p - 5050\theta_p/T ; A_p = \log [w_p \sigma_f \theta \nu \exp(\Delta S/k)] \quad (30)$$

In this form rates are in ( $\#/\text{cm}^2 - \text{sec}$ ), energies are in (ev) and temperature in ( $^{\circ}\text{K}$ ).

Figure 3 is a comparison of theory with experimental results for the system Cs-W. (9)

### CONCLUSIONS

The physical chemistry approach to the problem of theoretical correlations for the work function, desorption energies and desorption rates of intermetallic adsorption systems, yields results that are in good agreement with experimental data for Cs on different substrates as illustrated by Figures 1 through 3 and for other systems as discussed in references (1-3).

The derived correlations can be combined with Richardson's equation to establish electron emission S-curves for different adsorption systems. (13) These curves are also in agreement with experiment.

It is felt that the same approach will yield practical results for the case of gases adsorbed on metals. This problem is currently under investigation.

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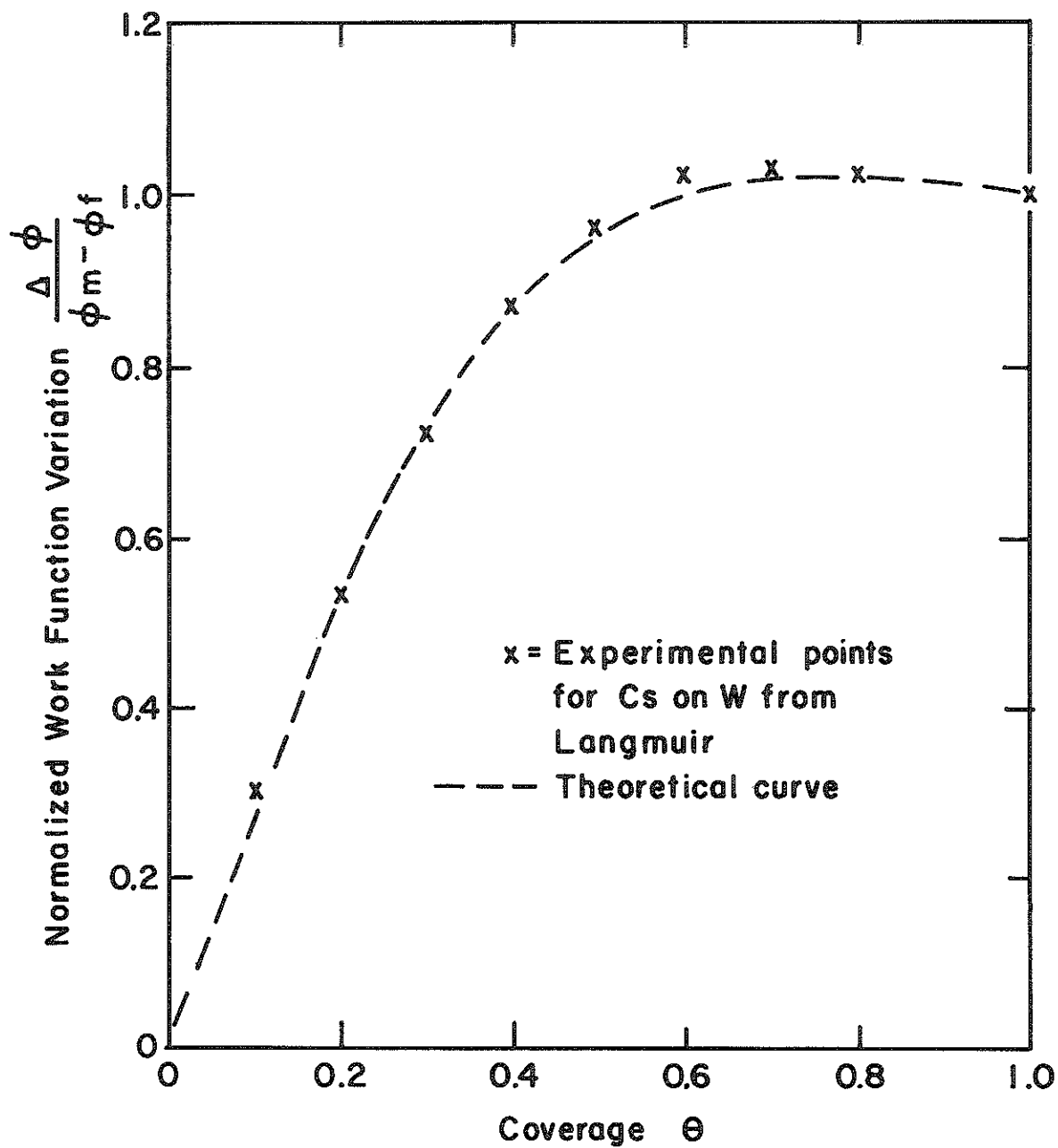


Figure 1

Theoretical curve and experimental data for the electron work function of tungsten coated by cesium.

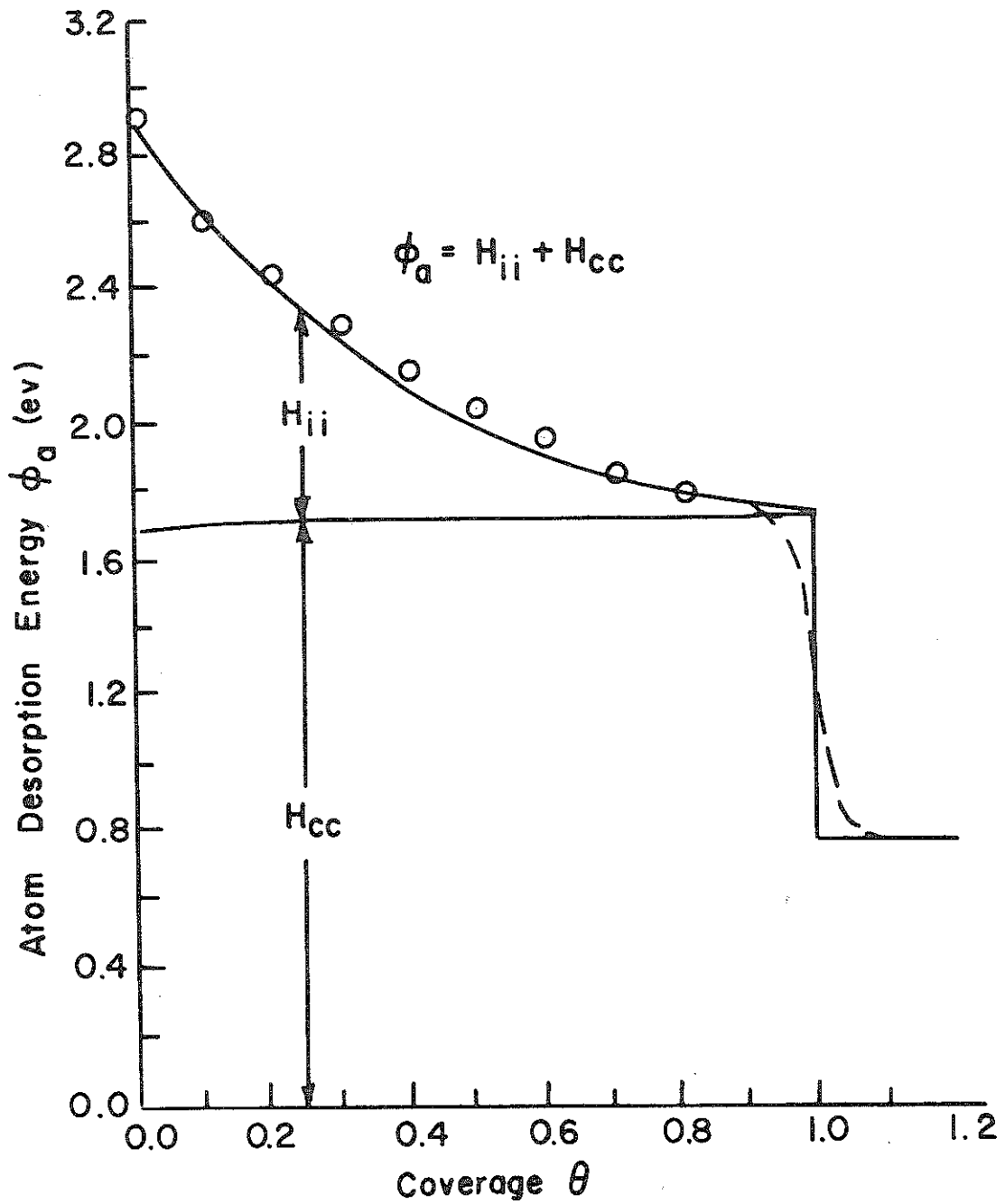


Figure 2

Theoretical curve and experimental data for the atom desorption energy from a tungsten surface coated by cesium.

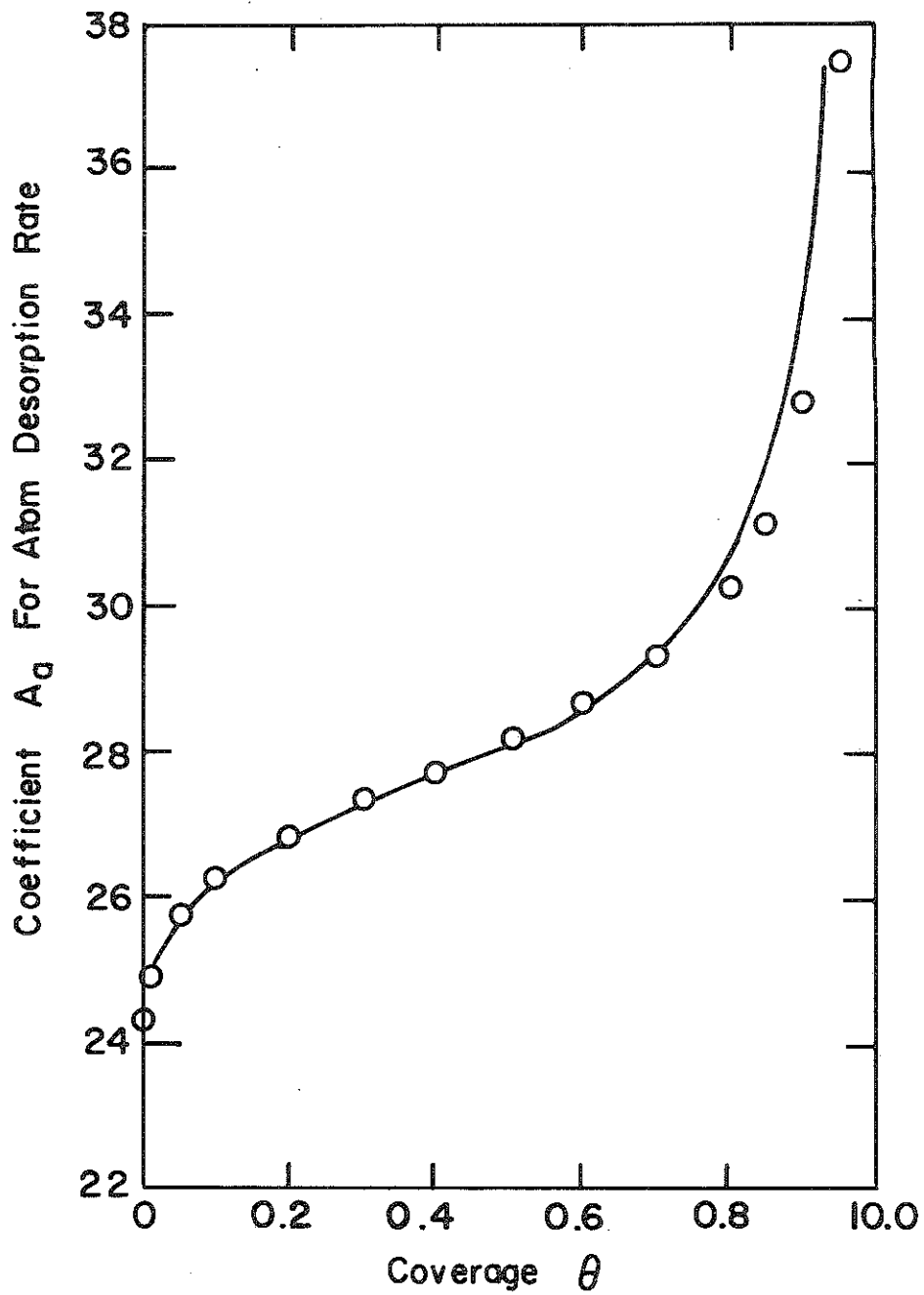


Figure 3

Theoretical curve and experimental data for the desorption rate constant  $A_a$  for tungsten coated by cesium.