ORBITAL ELECTRONEGATIVITY AND PHYSICAL PROPERTIES
OF METAL-GAS ADSORPTION SYSTEMS[*]

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SUMMARY

The concept of orbital electronegativity is extended to metals coated by electronegative adsorbates. Thus, each substrate atom on the coated surface is characterized by a neutral electronegativity which differs from that exhibited in the absence of the adsorbate. The neutral electronegativity is taken as linear function of the charge transfer arising from absorbate-substrate interactions. The amount of charge transferred is computed so that the adsorbate-substrate bond energy is maximum. Pairing of valence orbitals between neighboring adatoms is neglected. The reason is that, even at high coverage, the average distance between adatoms is much larger than the equilibrium distance characteristic of electronegative species in chemical combination.

Explicit relations are found for the work function and the desorption energy versus the degree of surface coverage. These expressions involve well defined properties of the adsorbate and substrate materials. A comparative investigation of the adsorption of different electronegative gases is presented. This investigation leads to two conclusions which are of particular interest to the technology of thermionic energy conversion.

(a) Oxygen adatoms are more tightly bonded to a given substrate surface than are any halogen adatoms.

(b) For the same density of adatoms on a given surface, oxygen gives rise to a higher work function change than does fluorine.

INTRODUCTION

The purpose of this paper is to present theoretical expressions for work functions of, and desorption energies from metal surfaces coated by electronegative adsorbates, i.e. oxygen and the halogens.

In an earlier paper,[1] work functions and desorption energies of bimetallic adsorption systems were described in terms of a chemical view of bonds on the bimetallic surface. The chemical description of surface bonds can be applied, not only to bimetallic surfaces, but also to other composite surfaces which exhibit desorption energies of chemical magnitude, i.e., ~ lev. The desorption energies of electronegative adsorbates from metal surfaces are of this order of magnitude. (Here, only the dissociative adsorption of the diatomic electronegative gases is considered.)

In this paper, the point of view advanced in reference 1 is applied to composite surfaces consisting of metals coated by electronegative adsorbates. Specifically:

(a) the work function of the composite surface is identified with the perturbed neutral (orbital) electronegativity of substrate, surface atoms; and

(b) surface bonds are viewed as chemical, and are assumed to arise from the pairing of valence orbitals.

Explicit relations are derived for the work function and the desorption energy versus the degree of surface coverage. The relations involve well defined properties of the adsorbate and substrate materials.

The body of this paper is arranged as follows. First, a chemical description of the bonds on the composite surface is given. Then, on the basis of this description, relations are derived for the work function and the desorption energy versus the degree of surface coverage. Finally, a comparative investigation of the adsorption of the gases is presented.

BONDS ON A METAL SURFACE COATED BY AN
ELECTRONEGATIVE ADSORBATE

The bonds formed on a metal surface coated by an electronegative adsorbate, denoted hereafter as a G-S surface, involve the pairing of valence orbitals between adsorbate and substrate atoms. Because the electronegativities of the pairing orbitals differ, these bonds are polar and are characterized by an amount of transferred charge, F.

The pairing of valence orbitals between neighboring atoms is negligible at all coverages of the electronegative adsorbates. This is so, because even at high coverages, the average distance between adatoms is much larger than the equilibrium distance characteristic of the electronegative species in chemical combinations. For example, the average distance between oxygen adatoms, assumed to be arranged on a square array, is 3.16 Å for a coverage of 10^{15} #/cm² (a very high coverage), while the equilibrium distance between oxygen atoms is 1.2 Å² in molecular oxygen.

WORK FUNCTION

The work function of a G-S surface is given by the perturbed neutral electronegativity of substrate atoms on the surface. This electronegativity equals that of the bare substrate, surface atoms plus the perturbation introduced by bond formation.[1] On the basis of the bond description presented earlier this perturbation is interpreted as follows.

The charge transferred, F, associated with the adsorbate-substrate bonds results in the formation of a dipole double layer at the surface. The double layer introduces an electrostatic potential which is superimposed on the electronegativity of the bare substrate, surface atoms. This potential is proportional to F. It follows that the work function, ϕ, of a G-S surface is given by the relation

$$\phi = \phi_s + bF \quad , \qquad (1)$$

where ϕ_s is the work function of the bare substrate, and bF is the electrostatic potential of the dipole double layer.

The coefficient b is given by the relation[1]

$$b = \frac{(0.905 \times 10^{-6})(v_f)(R \cos\beta)\, \sigma_f \theta}{(1+\alpha/R^3)(1+9\alpha\sigma_f^{3/2}\theta^{3/2})} \quad \text{ev/electron,} \qquad (2)$$

where all quantities have the same meaning as in reference 1. Notice that on G-S surfaces negative charge is transferred from the substrate to the adsorbate.

The number of bonding orbitals per adatom, v_f, is taken equal to the valence number of the electronegative adatom. Thus, v_f equals two for oxygen, and unity for fluorine or the other halogens. The bond length R is taken equal to the sum of the atomic radii[3], in cm, of the adsorbate and the substrate. The adsorbate surface density, σ_f, at full coverage, $\theta=1$, is in atoms/cm². The polarizability, α, in cm³, is taken as the sum of the polarizabilities of the adsorbate and the substrate. The individual polarizabilities are computed by Eq. 12 of reference 1 using n=1 for the electronegative species.

The quantity $\cos\beta$ depends on the geometric arrangement of the adsorbate on the substrate. For most adsorption systems a good estimate of $\cos\beta$ can be obtained by Eq. 13 of reference 1. However, for adsorbates of small size on planes of low surface density, e.g. oxygen on the (100) plane of tungsten, it is difficult to ascertain the geometric arrangement of the adsorbate on the substrate. For such situations $\cos\beta$ is estimated by assuming that the electronegative adsorbate rests on a hypothetical plane which is tangent to the subsurface atoms of the substrate. For example, this geometric arrangement is shown schematically in Fig. 1 for oxygen on the (100) plane of tungsten. In this figure all atoms are represented by hard spheres with radii equal to their respective atomic radii. It is emphasized that this method of estimating $\cos\beta$ is arbitrary. The only justification is that it proves expedient in a comparative investigation of the electronegative adsorbates which is presented later.

To compute the amount of charge transferred per bonding orbital of an adatom the adsorbate-substrate bond energy, D, is maximized with respect to F. For the electronegative adsorbates the energy D is given by the relation[1]

$$D = D_0\left(1-F^2/e^2\right)^{1/2} + \left(\frac{I_f + A_f}{2} - \phi_s\right)F - D_1 F^2/2e \quad , \qquad (3)$$

where use has been made of the relations

$$\phi_s = \frac{I_s + A_s}{2} \quad \text{(see reference 4)} \quad , \qquad (4)$$

$$D_1 = I_s - A_s + I_f - A_f - 2ke/R \qquad (5)$$
$$\text{(see reference 1)} \quad ,$$

D_0 is the energy of a purely covalent adsorbate-substrate bond, e is the charge of the electron, k is a coefficient which accounts for electrostatic repulsion between bonding orbitals, R is

the bond length, and I_i and A_i for i=f or s are the ionization potential and the electron affinity of the unperturbed valence orbitals, respectively. Note that the quantity $(I+A)/2$ is the neutral electronegativity[4] of a valence orbital.

The purely covalent bond energy, D_o, is computed by the approximate expression[5]

$$D_o = \frac{1}{2}\left[\frac{\lambda_s}{6} + D(G\text{-}G)\right] , \qquad (6)$$

where λ_s is the heat of sublimation of the substrate and $D(G\text{-}G)$ is the single bond energy of the electronegative gas molecule. The form of this approximate expression for the energy of a purely covalent electronegative adsorbate-substrate bond differs from that of the approximate expression, adopted in reference 1, for the energy of a purely covalent metallic adsorbate-substrate bond. Both forms have been used in molecular physics[6],[7] for the energy of a purely covalent heteroatomic bond. Presently there is no way of deciding which is more appropriate.

The energy D is maximized with respect to F when

$$\frac{dD}{dF} = 0 , \qquad (7)$$

or, after some elementary algebra, when

$$F/e = \frac{(I_f + A_f)/2 - \phi_s}{(D_o/e)(1-F^2/o^2)^{-1/2} + D_1} , \qquad (8)$$

Equation 8 can be solved for F provided that the values of the quantities I_f, A_f and D_1 (Eq. 5) are known for the system under consideration. Spectroscopically derived values of the ionization potentials and electron affinities of oxygen and the halogens are given in reference 8. Using these values for I_f and A_f, the quantity D_1 is estimated by method (b) of reference 1*, namely by taking

$$k = 1, \quad I_s - A_s = c_1\phi_s \text{ and } c_1 = 1.3 . \qquad (9)$$

In summary, the work function of a G-S surface is given by the relation

$$\phi = \phi_s + bF ,$$

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*It is pointed out that this method, i. e. Eq. 9, for estimating the value of D_1 proved to be quite useful for the systems considered in reference 1.

where

$$b = \frac{(0.905\times10^{-6})(v_f)(R\cos\beta)\ \sigma_f\theta}{(1+\alpha/R^3)(1+9\alpha\sigma_f^{3/2}\theta^{3/2})} \quad \text{ev/electron},$$

and

$$F/e = \frac{(I_f + A_f)/2 - \phi_s}{(D_o/e)(1-F^2/e^2)^{-1/2} + D_1} .$$

Note that at $\theta = 0$, $b = 0$ and ϕ equals the bare substrate work function, ϕ_s.

DESORPTION ENERGY

The desorption energy, E_d, of electronegative adatoms from a G-S surface is simply the bond energy, D, times the number of bonds, v_f. Therefore, E_d, is given by the relation

$$E_d = v_f D , \qquad (10)$$

where

$$D = \frac{1}{2}\left[\frac{\lambda_s}{6} + D(G\text{-}G)\right](1-F^2/e^2)^{1/2}$$
$$+ \left(\frac{I_f + A_f}{2} - \phi_s\right)F - D_1F^2/2e ,$$

and F satisfies Eq. 8.

RESULTS

A number of investigators[9]-[13] have measured work functions and desorption energies of G-S adsorption systems. However, these investigators do not report surface coverages, and therefore, a detailed comparison between the experimental data and the expressions derived here cannot be made. For this reason, the derived relations are used in a comparative investigation of the electronegative adsorbates.

Work functions and desorption energies versus degree of surface coverage have been computed for the adsorption system O-W(100), i.e., oxygen on the (100) plane of tungsten, F-W(100), Cl-W(100), Br-W(100), and I-W(100). The results are presented in Figs. 2 and 3, and in Table 2. For the calculations, the following numerical data are used:

(a) The adsorbate properties are given in Table 1, and the substrate properties are $\phi_s = 4.60$ ev,[4] $\lambda_s = 8.68$ ev,[1] $r_s^* = 1.35\text{Å}$,[3] and $\alpha_s = 4.06\text{Å}^3$.[1]

(b) The quantity D_1 (Eq. 5) was calculated using the tabulated values of I_f and A_f (see Table 1), and Eq. 9.

(c) The adsorbate surface density, σ_f, at full coverage, $\theta=1$, was taken as $10^{15} \#/cm^2$ for each system. This value corresponds to a 1:1 ratio of atoms to substrate atoms on the (100) plane of tungsten. This choice of σ_f is somewhat arbitrary, but it is reasonable for a comparative study.

(d) The quantity $\cos\beta$ was computed by Eq. 13[†] of reference 1 for the adsorbates chlorine, bromine and iodine. For the adsorbates oxygen and fluorine, the alternate proceedure described earlier was used to estimate $\cos\beta$.

The figures include the computed values of $\cos\beta$, D_o, and D_1.

Plots of the work function of tungsten versus oxygen and fluorine coverage are shown in Fig. 2. It is seen from this figure that for a given degree of coverage, oxygen adsorption results in a work function increase which is about twice as large as that which results from fluorine adsorption. The reason for this is that each oxygen adatom forms two adsorbate-substrate bonds while each fluorine adatom forms only one adsorbate-substrate bond. Thus, although the neutral electronegativity, i.e. $(I+A)/2$, of a fluorine valence orbital exceeds that of an oxygen valence orbital, (see column five of Table 1) the effective dipole moment per oxygen adatom exceeds that per fluorine adatom. This observation is consistent with the recent experiments of Lieb and Kitrilakis.[11]

The estimated increase of work function of the oxygenated tungsten (100) plane is about 1.15 ev. It is noted that the experiments of Engelmaier and Stickney[9] indicate that oxygen adsorption on the (100) plane of tungsten increases the work function by at least 0.8 ev.

Plots of the work function of tungsten covered by the different halogens are shown in Fig. 3. It is seen from this figure that although the neutral electronegativities of the valence orbitals of the halogens decrease in the order

$$F_2 > Cl_2 > Br_2 > I_2 \quad \text{(see column five of Table 1)} \quad,$$

the effectiveness of the halogens in increasing the work function of tungsten is in the reverse order, namely

$$I_2 > Br_2 > Cl_2 > F_2 \quad.$$

The reason is that the atomic radii and the quantity $R \cos\beta$ (see Eq. 2) decrease in the order

$$I_2 > Br_2 > Cl_2 > F_2 \quad.$$

Regarding desorption energies, it is noted that since the amount of charge transferred F (Eq. 8) is independent of coverage, these energies (Eq. 10) are also independent of coverage. At present, there are not sufficient experimental data to test the validity of this result. However, the experiments of Zingerman and Ishchuk[12] did show that the desorption energy of oxygen adatoms from the (110) plane of tungsten is independent of coverage in the range $0.1 \leq \theta \leq 0.9$.

Estimated desorption energies of adatoms for different G-S systems are presented in Table 2. The following observations can be made with regard to these energies.

(a) The estimated desorption energy of oxygen is considerably higher than that of any halogen. The reason is that each oxygen adatom forms two adsorbate-substrate bonds, while each halogen adatom forms only one adsorbate-substrate bond. Experimentally, it is also found that the desorption energy of oxygen from tungsten is significantly higher than that of either chlorine or fluorine from tungsten.[9-11]

(b) The crystallographic orientation of the surface does affect the value of the estimated desorption energy, e.g. E_d for the O-W(100) system is 0.8 ev higher than E_d for the O-W(110) system. Formally, this is due to the difference of neutral electronegativities, i.e. work functions, of the two planes.

(c) The estimated desorption energies of halogen adatoms decrease in the order

$$F_2 > Cl_2 > Br_2 > Cl_2 \quad.$$

This is the same order as that of the neutral electronegativities of the valence orbitals.

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[*] This quantity is the atomic radius of the substrate.

[†] In this calculation the substrate surface density, σ_s, is $10^{15} \#/cm^2$, i.e., the surface density of the (100) plane of tungsten.

Finally, it is pointed out that it is difficult to determine experimentally whether electronegative adatoms desorb as atoms or as molecules. Equation 10 gives the desorption energy for atoms. The desorption energy for molecules is simply twice E_d, Eq. 10, minus the energy of dissociation of the electronegative gas molecule. The expressions derived here may be helpful in determining the form of the desorbed species. For example, if the variation of the work function with surface coverage, and the geometric arrangement of the adsorbate on the substrate are known experimentally, the quantity D_1 can be fixed. With this value of D_1, the desorption energies for atoms or molecules can be computed by means of Eq. 10. The computed values can then be compared with the experimental value of the desorption energy. The relative magnitudes of the computed and experimental desorption energies may indicate whether the adatoms desorb as atoms or as molecules.

CONCLUDING REMARKS

A chemical view of bonds on surfaces, and the concept of orbital electronegativity have been used to derive relations for work functions, and desorption energies versus degree of surface coverage, of any G-S adsorption system. These expressions have been used for a comparative study of the electronegative adsorbates, i.e. O_2, F_2, etc., on the (100) plane of tungsten. Although the estimated work functions and desorption energies reported in this study represent approximate values, they lead to two general conclusions which are of particular interest to the technology of thermionic energy conversion.

(a) Oxygen adatoms are more tightly bonded to a given substrate surface than are any halogen adatoms.

(b) For the same density of adatoms on a given surface, oxygen gives rise to a higher work function than does fluorine.

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Table 1
Electronegative Adsorbate Properties Used in Theoretical Calculations

Adsorbate	Number of Bonding Orbitals, v_f	Atomic[3] Radius, r_f(Å)	Polarizability, α_f(Å³)	Ionization Potential, I_f[8] Electron Affinity, A_f		Single Bond[7] Energy D(G-G) (ev)
				$\frac{I_f+A_f}{2}$ (ev)*	I_f-A_f (ev)	
Oxygen	2	0.6	0.216	9.65**	15.27**	1.52
Fluorine	1	0.5	0.125	12.18	17.36	1.56
Chlorine	1	1.00	1.00	9.38	11.30	2.48
Bromine	1	1.15	1.52	8.40	9.40	1.97
Iodine	1	1.40	2.74	8.10	9.15	1.54

* This quantity is the neutral electronegativity of an adsorbate valence orbital.

** These values correspond to the p orbital ionization potentials and electron affinities.

Table 2
Estimated Desorption Energies

System	E_d (ev)
O-W(100)	6.08
O-W(110)	5.28*
F-W(100)	4.49
Cl-W(100)	3.53
Br-W(100)	2.94
I-W(100)	2.45

* In this calculation, the work function, ϕ_s, is taken equal to 5.3 ev.
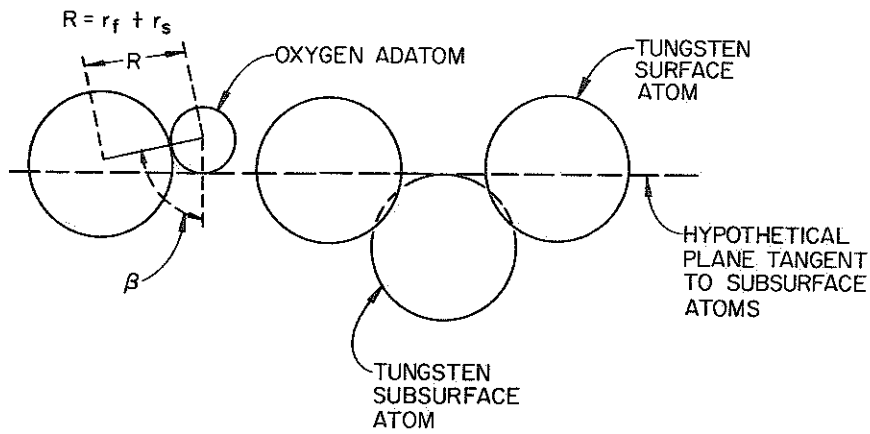
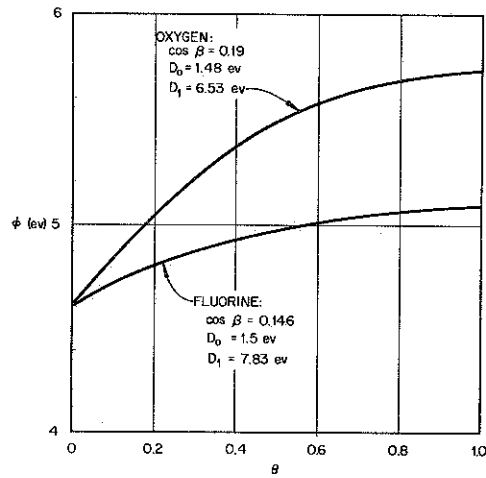Figure 1.   Schematic showing hypothetical geometric arrangement of an oxygen adatom on the (100) plane of tungsten.

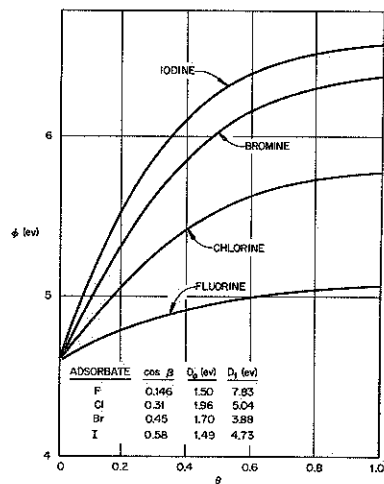Figure 2.   Theoretical work function, ϕ, versus coverage, θ, for O-W(100) and F-W(100) systems.

Figure 3.   Theoretical work function, ϕ, versus coverage, θ, for F-W(100), Cl-W(100), Br-W(100) and I-W(100) systems.

VACUUM WORK FUNCTION OF OSMIUM*

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SUMMARY

The thermionic electron emission from three Os balls was measured in high vacuum using a novel spherical geometry. The average zero-field Richardson constants were determined to be $A_r = 120 \pm 40$ amp/cm^2°K^2, $\phi_r = 5.24 \pm 0.05$ e.v. Extensive flashing at 2600°K did not alter the emission. A few measurements were also made on Ir samples, some of which showed low-ϕ contaminants not removed by a 3-min. flash at 2565°K.

Introduction

Prior to the present measurements three widely-differing values for the vacuum work function of Os existed, any one of which could have been correct. Houston and Dederick[1] had measured the thermionic emission of an Os-plated W filament, both in vacuum ($\phi \approx 5.16$ e.v.) and in Cs vapor. The emission in Cs vapor lay between that of Ir and Re indicating (according to the Rasor-Warner model[2]) a vacuum work function between that of Ir (5.3 e.v.) and Re (4.9 e.v.). Then Wilson[3] published a value for the vacuum work function of Os of 4.83 e.v., using a sample that had been flashed to only 1680°K. Next, Zalm and vanStratum[4] briefly described a photoelectric determination of the vacuum work function of Os, which yielded $\phi = 5.93$ e.v. However, they gave no details on sample cleanliness.

The present research was undertaken to obtain a definitive value for the vacuum work function of Os. A problem immediately arose, however, in that Os cannot be fabricated in filamentary form, which is the geometry usually used in measurements of thermionic work function. One could, of course, have electroplated Os onto a W filament, but then the same questions about possible interdiffusion or plating-bath contamination can be raised, which would leave the matter not definitely resolved.

Therefore, it was decided to make the measurements using a novel technique** in which the emitting sample has the geometry of a hanging drop. Such a sample geometry can be produced by electron bombarding an Os rod in high vacuum until its lower end melts. Upon freezing, the "droplet" is found to have a nearly-spherical shape with a smooth shiny surface. Figure 1 is a photograph of Os ball #1 (average diam. = 3.00 mm) which was produced on the end of a sintered rod of Os. The balls are usually composed of a small number of crystals. After extensive heating (below the melting point) the grain boundaries become faintly visible because of thermal etching. A few grain boundaries are visible in Fig. 1, as well as a reflection of the camera lens used to take the picture.

The next problem was how to heat the ball to high temperature and yet measure the electron emission from a well-defined emitting area. A technique was devised in which the ball was placed in a hemispherical anode (essentially at ground potential) and run at a potential composed of a D.C. plus an A.C. voltage. During most of a cycle the ball was heated by electron bombardment from an adjacent filament. During the remainder of the cycle, the electric field reversed, and emitted electrons were then accelerated from the ball to the anode. By electrically isolating part of the anode, the emission from a well-defined emitting area could be measured with an oscilloscope.

This technique has several advantages: (1) Many metals cannot be heated to a very high temperature in filamentary form because of low tensile strength at high temperatures. This is not a limit

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