# ADSORPTION PHYSICS OF METALLIC SURFACES PARTIALLY COVERED BY METALLIC PARTICLES. I ATOM AND ION DESORPTION ENERGIES

#### J. D. LEVINE\* and E. P. GYFTOPOULOS

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

#### Received 9 October 1963

The desorption energies of atoms and ions for metallic surfaces partially covered by monatomic metallic particles are theoretically calculated. The calculation is based on the assumptions that the adsorbed particles consist of a single species held onto the surface by bonds that are partially ionic and partially covalent.

The theoretical results are compared with available experimental data and very good agreement between theory and experiment is established.

A unique feature of the derived formulas is that they do not involve any adjustable constants.

#### 1. Introduction

The physical properties of metallic surfaces, partially covered by dissimilar metallic particles, are different from the properties of pure surfaces of either material. This fact has been investigated by many authors and plays an important role in the fields of general surface physics and thermionic energy conversion.

The physical properties of interest are the electron work function, the atom and ion desorption energies and the rates of electron, ion and atom emission. In general, these properties depend on the degree of coverage of the surface, the temperatures of the surface and the metallic vapor, the electrostatic potential prevailing in the vicinity of the surface and the physical parameters of the materials involved.

Even though physical properties of composite surfaces have been studied extensively experimentally, the theoretical correlations that have been proposed for the changes induced by the adsorbed particles are incomplete.

In a previous communication<sup>1</sup>), the authors presented a theoretical cor-\* Present Address: RCA Laboratories, Princeton, N.J. relation between electron work function, the degree of coverage and the material properties of composite surfaces. This correlation was based on an extension of physical concepts developed in molecular physics to the field of adsorption physics. No adjustable contants were used.

The purpose of the present effort, which will be described in three separate papers, is to derive theoretical correlations for other physical properties of interest and their dependencies on the various thermodynamic variables and material properties that characterize the composite surface. Specifically, in part I, the atom and ion desorption energies are calculated, in part II theoretical correlations for the rates of ion and atom emission are presented and in part III electron emission S-curves are derived.

This is the first paper of the series and is concerned with the theoretical calculation of the desorption energies of atoms and ions for composite surfaces. The paper is organized as follows. First, an outline of the surface system and the desorption problem under consideration is given. Second, a brief review of previous approaches to the problem is presented. Third, desorption energies of atoms and ions are derived theoretically. Finally, the derived correlations are compared with available experimental results and excellent agreement between theory and experiment is established.

A unique feature of the derived theoretical calculations is that they do not involve any adjustable constants.

The study is applicable only to metallic surfaces immersed in monatomic metallic vapors. This restriction results in some both simplifying and practical features of the problem which are not present in other adsorption systems. First, the adsorption bond is strong and similar to the familiar chemical bond. Thus, the adsorbed particles are probably "chemi-sorbed" rather than "physically adsorbed" as in the case, for example, of noble gases adsorbed on metals. Second, only monatomic particles are adsorbed or desorbed. This feature simplifies the calculations of the energies and rates of desorption. Third, all incident particles are immediately adsorbed without reflections  $^{2-4}$ ). This feature is not present in systems involving diatomic molecules. Finally, metallic particles adsorbed on metals may be re-emitted as ions. This feature is not found in other adsorption systems and it has important practical implications in thermionic energy conversion and other fields of physical electronics.

#### 2. Desorption energies of composite surfaces

#### 2.1. GENERAL REMARKS AND BRIEF LITERATURE REVIEW

The adsorption system under consideration is a pure metallic surface at temperature T immersed in a dissimilar monatomic metallic vapor bath

at temperature T'. When dynamic equilibrium is established, a fraction  $\vartheta$  of the surface is covered by adsorbed particles.

The desorption energy  $\varphi_a$  of an atom is defined as the potential energy difference required to remove an adsorbed particle from the composite surface, in the form of a free atom. The desorption energy  $\varphi_p$  of an ion is defined as the potential energy difference required to remove an adsorbed particle from the composite surface, in the form of a free ion.\* These potential energies are in general functions of  $\vartheta$  because of surface interactions. In addition, there may be a slight explicit dependence on T through the small thermal expansions of the substrate lattice parameters, but this dependence is usually considered a second order effect and is neglected.

Many investigators have derived theoretical or semi-empirical expressions for  $\varphi_a$  and  $\varphi_p$  as functions of  $\vartheta$  and the properties of the materials involved. Their work can be classified into three main groups according to the particular surface model used for the calculations.

The first group<sup>5–7</sup>) attempts to solve the problem by means of quantum mechanical wave functions of the periodic lattice structure of the surface. The results, however, are only grossly qualitative.

The second group  $^{8-11}$ ) considers the surface as a conducting plane and assumes that the adsorbed particles exist in two distinct species, namely, as pure ions and as pure atoms. It is felt that this model has some fundamental shortcomings. First, in the derivations it is necessary to make extensive use of the concept of the classical image force which is questionable at interatomic distances. Second, the model implies that the adsorbate particles have a sharply defined valence energy level. This is also questionable since quantum mechanical calculations show that the valence level is broadened, due to interactions, when the adsorbate particle is near the metal surface<sup>12,13</sup>). Hence, according to quantum mechanics, one would expect to find at the surface a mixture of ionic and covalent bonds rather than separate purely ionic or purely covalent bonds. Third, the model implies that vapor particles with low ionization potentials V<sub>f</sub> should be adsorbed primarily as ions, while those with high ionization potentials should be adsorbed primarily as atoms. This implication seems incorrect because electron work function variations of tungsten coated by cesium ( $V_f = 3.87 \text{ eV}$ ) or thorium  $(V_{\rm f} = 6.7 \, {\rm eV})$  have been experimentally found to be similar<sup>1</sup>).

The third group  $^{2, 3, 14-20}$ ) proposes a surface model in which the adsorbed particles exist only as a single species bound to the surface by polarized or partially ionic and partially covalent bonds. The single adsorbed species

<sup>\*</sup>  $\varphi_a$  and  $\varphi_p$  should not be confused with the enthalpies or internal energies of desorption which differ from  $\varphi_a$  and  $\varphi_p$  by terms of the order of kT.

can be desorbed, however, either as a free atom or free ion. Although these workers have made much progress in the understanding of surface physics, they have not yet achieved the goal of calculating desorption energies as functions of the degree of coverage and the properties of the pure substrate and adsorbate materials, *without using adjustable parameters*.

It is felt that the model of single species of adsorbed particles\* is worth further exploration and it is proposed as the basic model for the purpose of calculating desorption energies of atoms or ions from composite surfaces. The mixed or "chemical" nature of the bond of metallic particles adsorbed on metallic surfaces is suggested both by the quantum mechanical broadening of the valence energy level of the adsorbed particles and by the strength of the bond (bond energy greater than 1 eV).

The ideal approach to the problem of calculation of desorption energies would be to treat the chemical surface bond quantum mechanically. This is, however, an extremely difficult task and so far has not yielded any practical results, as already indicated. An alternate procedure is to treat the problem macroscopically by making use of certain analogies that exist between the concepts of adsorption and molecular physics. For example, sublimation is analogous to rupture of a diatomic molecule consisting of similar atoms; desorption is analogous to the rupture of a diatomic molecule composed of dissimilar atoms; electron work function is analogous to ionization potential or to electronegativity, etc. How these analogies are implemented, in order to calculate the desorption energies, is described in the following sections.

#### 2.2. Calculation of the desorption energy $\varphi_a$

In molecular physics, a chemical bond is in general considered as partly ionic and partly covalent<sup>21-25</sup>). By direct extension, intermetallic surface bonds may also be considered as partly ionic and partly covalent, and the desorption energy  $\varphi_a$  of atoms may be assumed as consisting of an ionic and a covalent part:

$$\varphi_{a} = H_{ii} + H_{cc} \tag{1}$$

where  $H_{ii}$  is the ionic and  $H_{cc}$  the covalent contributions, respectively. Equations of the same form as eq. (1) have been used for diatomic molecules<sup>21</sup>), for semiconductors<sup>26</sup>) and for gases adsorbed on metals<sup>14,15</sup>). It is usually presumed that  $H_{ii}$  arises from a Coulomb attraction between opposite charges at opposite ends of the bond, and that  $H_{cc}$  arises from pairing of valence electrons contributed by the atoms in the bond. Thus, a purely ionic bond may be characterized by a dipole moment equal to the product

<sup>\*</sup> The terminology "adsorbed particles" is advisedly introduced to avoid confusion with the "adatoms" and "adions" of the two-species-model.

of the electric charge times the internuclear distance, while a purely covalent bond has a zero dipole moment.

Admittedly, the separation of the desorption energy into an ionic and a covalent part overlooks resonance effects. The reason for this oversight are the difficulties encountered in the computation of the resonance energy. It may be argued, however, that the surface wave function is expanded into two orthogonal energy wave-functions and that the ionic and covalent contributions are exactly the eigenvalues of these functions.

The question now is: how does one calculate  $H_{ii}$  and  $H_{cc}$ ? Clearly, whatever technique is used for this purpose, at least three conditions must be met to have a satisfactory answer. First,  $H_{ii}$  must vanish for a purely covalent bond. Second,  $H_{cc}$  must vanish for a purely ionic bond. Third, when material X is adsorbed on bulk material X,  $H_{cc}$  must reduce to the heat of sublimation of material X. Other workers do not include all three.

### 2.2.1. Calculation of $H_{ii}$

The ionic contribution  $H_{ii}$  to the desorption energy  $\varphi_a$  is assumed to arise from a fraction of charge F of the adsorbate which is transferred to the substrate. The fraction F determines the partial ionic character of the bond and is associated with the surface dipole moment. The value of  $H_{ii}$ can be calculated through the following thought process. First, remove an adsorbed particle with a fractional charge F to infinity, leaving in the substrate an equal and opposite charge. This step requires an amount of coulomb energy equal to  $F^2 e^2/R$  where e is the unit electric charge and R is the internuclear distance between substrate and adsorbate particles. The internuclear distance is taken equal to the sum of the covalent radii\*. Next, remove the fractional electronic charge from the surface to infinity. This step requires an amount of energy  $F\varphi_e$  where  $\varphi_e$  is the electron work function of the composite surface. The fraction F appears to the first power here because the presence or absence of an electron from the surface does not alter the work function of the surface. Finally, combine the fractional ion with the fractional electron to produce a neutral atom. This step releases an amount of energy equal to  $F^2 V_f$  where  $V_f$  is the ionization potential of the adsorbate and  $F^2$  appears because ionization is a coulomb interaction. Summation of all the energies involved in the thought process results in

$$H_{\rm ii} = F \varphi_{\rm e} [1 + \delta] \tag{2}$$

where

$$\delta = F(e^2/R - V_{\rm f})/\varphi_{\rm e}.$$
(3)

\* For a detailed description of the arrangement of the adsorbed particles on the surface see ref. 1.

Note that, for F = 1,  $H_{ii}$  reduces to the energy required to remove an adsorbed ion from the surface, as it should, and it is similar to the equation proposed by others<sup>8, 9, 11</sup>) for the same purpose. Note also that, for F = 0, namely when there is no dipole moment and the bond is purely covalent,  $H_{ii}$  reduces to zero, as it should. Typical numerical calculations show that  $\delta$  is very small (rarely greater than 0.03) so that the expression for  $H_{ii}$  can be approximated by:

$$H_{\rm ii} \approx F \varphi_{\rm e}$$
 (4)

Nevertheless, eq. (2) will be used in all subsequent computations.

The electron work function  $\varphi_e$  as a function of coverage and material properties of adsorbate and substrate has already been calculated<sup>1</sup>). The calculation is based on a detailed surface model which accounts both for the chemical structure (electronegativity) variation and for the dipole moment variation with coverage. The result is reproduced below\* (c.g.s. units) without redefining the symbols.

$$\varphi_{e} = \underbrace{\varphi_{m} - (\varphi_{m} - \varphi_{f})(1 - G(9))}_{\text{chemical structure}} = \underbrace{\frac{0.76 \times 10^{-14} \sigma_{f} \cos \beta (\varphi_{m} - \varphi_{f}) 9G(9)}{(1 + \alpha/R^{3})(1 + 9\alpha\sigma_{f}^{\frac{3}{2}}9^{\frac{3}{2}})}_{\text{dipole moment}} (5)$$

The fraction of charge F is not uniquely definable but can be inferred from the dipole moment part of  $\varphi_e$ . Indeed, this part is due to a surface double layer of thickness  $R\cos\beta$ . According to the discussion in ref. 1, the dipole moment (in esu  $\cdot$  cm) of the double layer is

$$M_1 = 2.03 \times 10^{-18} \cos \beta (\varphi_{\rm m} - \varphi_{\rm f}) G(9)$$
(6)

if no self-depolarization or surface diple-dipole interactions are taken into account. On the other hand, if self-depolarization is considered, then the dipole moment is reduced to

$$M_2 = M_1 / (1 + \alpha / R^3)$$
(7)

<sup>\*</sup> The insensitivity of  $\varphi_e$  to the exact value of the shape factor  $G(\vartheta)$  has not been stressed in ref. 1. This factor was derived to account only for the behavior of work function at  $\theta = 0$  and 1. It turns out, however, that in cases where  $\varphi_e$  becomes equal to  $\varphi_m$ for  $0 < \vartheta < 1$ , the value of  $\vartheta$  at which this occurs is independent of  $G(\vartheta)$  and depends only on the material properties of the substrate and the adsorbate. This is an additional reason why theoretical and experimental values of  $\varphi_e$  agree so well over the entire range of coverage.

and if both self-depolarization and dipole-dipole interactions are included, the dipole moment is further reduced to

$$M_3 = M_2 / (1 + 9 \alpha \sigma_f^2 \, 9^{\frac{3}{2}}). \tag{8}$$

The fraction F may be associated with  $M_1$ ,  $M_2$  or  $M_3$  because it is not possible to ascertain whether self-depolarization and/or dipole-dipole interactions result in a net charge transfer from the substrate to the adsorbate, or whether the adsorbate is simply polarized with no charge transfer. In view of this ambiguity and the recognition that the assumed localization of the charge fraction F is already an approximation, it is arbitrarily postulated that Fis associated with  $M_2$ , i.e.

$$F = \frac{M_2}{eR\cos\beta} = \frac{0.422(\varphi_{\rm m} - \varphi_{\rm f})G(\theta)}{R(1 + \alpha/R^3)}$$
(9)

In eq. (9), F is in correct dimensionless units if  $(\varphi_m - \varphi_f)$  is given in eV, R is given in angstroms, and  $\alpha$  is given in cubic angstroms. Note that if instead of  $M_2$  the dipole moments  $M_1$  or  $M_3$  were used for the calculation of F, then the values of  $\varphi_a$  would not be appreciably altered.

Thus the theoretical calculation of  $H_{ii}$  is completed because all terms in eq. (2) are either known physical constants or calculated functions. In particular, the numerical constants in eqs. (5) and (9) are theoretically calculated; they are not determined from adsorption data. Also note that eq. (2) appears in a very simple form because all the complicated surface interactions are hidden in the coverage-dependent quantities  $\varphi_e$  and F.

# 2.2.2. Calculation of $H_{cc}$

The covalent contribution to  $\varphi_a$  is assumed to arise from the mutual pairing of the valence spins of the substrate and adsorbate particles.

The exact calculation of  $H_{cc}$  is extremely difficult because, even for simple diatomic molecules, standard theoretical approximations to Schrödinger's equation result in covalent energies that are grossly different from experimental results<sup>27</sup>). Nevertheless, it is possible to arrive at an estimate of  $H_{cc}$  by formulating an expression that reflects various features of covalent bonds that have been previously established in molecular physics.

Since  $H_{cc}$  arises from pairing of valence charges, the substrate and the adsorbate must each contribute to the bond.

Consider first the adsorbate (sometimes called film material) which is denoted by the subscript f. Its contribution to the covalent part of the desorption energy is assumed proportional to the heat of sublimation  $\varphi'_{\rm f}$ , to the square of the angular strength  $S_f$  of the valence orbital, and to the valence charge  $q_f$ . The reasons for including these three dependencies are given below.

The heat of sublimation  $\varphi'_f$  is included to assure that, when the adsorbate is adsorbed on its own bulk material,  $H_{cc}$  reduces to  $\varphi'_f$ . The idea of choosing a characteristic energy by appealing to a known limiting condition has been first successfully used by Pauling in his treatment of diatomic molecules<sup>21</sup>.

The angular strength squared,  $S_f^2$ , appears because the greater the eccentricity of the wave function of the valence orbital, the larger the overlapping of the electron clouds of the surface particles and the stronger the covalent bond. The  $S_f^2$  concept has been extensively used by Pauling<sup>28</sup>) Hultgren<sup>29</sup>) and others. The value of  $S_f$  depends on the s, p or d nature of the valence orbitals participating in the bond. Typical S values are indicated in the appendix.

The valence charge,  $q_f$ , participating in the covalent bond is purposely included to satisfy the required condition that when  $q_f = 0$  a purely ionic bond is formed and  $H_{cc}$  should vanish. Other workers have used expressions for  $H_{cc}$  that are independent of charge, so they have not satisfied this condition. The first power of  $q_f$  is chosen because single, double, or triple covalent bond energies are approximately in the ratio 1:2:3, and, as it will become evident shortly, the final result for  $H_{cc}$  is insensitive to the exact power of  $q_f$ .

In summary, the contribution of the adsorbate to the covalent part of the bond energy is assumed proportional to  $\varphi'_f S_f^2 q_f$ . For similar reasons, the contribution of the substrate metal is assumed proportional to  $\varphi'_m S_m^2 q_m$ . The simplest relationship which combines these two contributions and which guarantees the necessary limiting requirements  $-H_{cc} = \varphi'_f$  for m = f, and  $H_{cc} = 0$  for  $q_f = 0$  – is the normalized geometric mean:

$$H_{\rm cc} = \left[ \varphi_{\rm f}' \varphi_{\rm m}' \cdot \frac{4 \, S_{\rm f}^2 S_{\rm m}^2}{(S_{\rm f}^2 + S_{\rm m}^2)^2} \cdot \frac{4 \, q_{\rm f} q_{\rm m}}{(q_{\rm f} + q_{\rm m})^2} \right]^{\frac{1}{2}} \tag{10}$$

Note that an arithmetic mean would not be correct because then  $H_{cc} \neq 0$  when  $q_f = 0$ .

The q dependence in this equation can be further simplified by the introduction of the approximate relationships  $q_f = v - F$ ;  $q_m = v + F$  where v is the largest number of valence electrons that can participate in the covalent bond. Since this number is limited by the adsorbate particles rather than the substrate, which provides a reservoir of free electrons, v is taken equal to the number of valence electrons initially present in a free adsorbate particle. For example, for alkali metals v = 1 and for alkaline earths v = 2. Thus:

$$H_{\rm cc} = \left(\varphi_{\rm f}'\varphi_{\rm m}'\right)^{\frac{1}{2}}S_{\rm fm}Q_{\rm fm} \tag{11}$$

where  $S_{\rm fm} = 2/(S_{\rm f}/S_{\rm m} + S_{\rm m}/S_{\rm f})$  and  $Q_{\rm fm} = (1 - F^2/v^2)^{\frac{1}{2}}$ . The first factor in eq. (11),  $(\varphi'_{\rm m}\varphi'_{\rm f})^{\frac{1}{2}}$ , has the dimensions of energy. This factor is completely analogous to Pauling's well established expression  $\sqrt{(D_{AA}D_{BB})}$  for the covalent energy of diatomic molecules<sup>21</sup>). The second factor,  $S_{\rm fm}$ , is dimensionless and may be interpreted as the angular efficiency of the orbitals. For identical orbitals  $S_{\rm fm} = 1$  and for different orbitals it is smaller than unity. The third factor,  $Q_{\rm fm}$ , is also dimensionless and may be interpreted as the charge efficiency. The charge efficiency is unity when the bond is purely covalent (F = 0) and it is equal to zero when the bond is purely ionic, i.e., the entire valence charge is transferred from the adsorbate to the substrate (F = v). The angular and charge efficiencies correctly suggest that perfect electron pairing in a covalent bond occurs only when the pairing orbitals are identical and have equal charges. Departure from these equalities weakens  $H_{cc}$ .

Even though the calculation of  $H_{cc}$  has been based on proportionalities, the final result (eq. 11) does not contain any arbitrary or adjustable constants. This is achieved through the normalization which reflects the necessary requirements that  $H_{cc} = \varphi'_f$  for m = f and  $H_{cc} = 0$  for v = F.

This completes the calculation of the covalent contribution to the desorption energy  $\varphi_a$ .

Combination of eqs. (2) and (11) yields:

$$\varphi_{a} = \underbrace{F\varphi_{e}(1+\delta)}_{\text{ionic part}} + \underbrace{(\varphi_{f}'\varphi_{m}')^{\frac{1}{2}}S_{fm}Q_{fm}}_{\text{covalent part}}$$
(12)

This is the theoretical expression for the desorption energy of atoms that was sought. As already emphasized, it incorporates the limiting conditions for purely ionic or covalent bonds and reduces to the heat of sublimation of the adsorbate when the latter is adsorbed on its own material. In addition,  $\varphi_a$  is explicitly related to the degree of coverage  $\vartheta$  and the material properties of the substrate and the adsorbate. The latter dependence is introduced through  $\varphi_e$  and F (eqs. (5) and (9)).

#### 2.3. CALCULATION OF THE DESORPTION ENERGY

The desorption energy  $\varphi_p$  of an ion can be derived from  $\varphi_a$  by means of a usual simple thought process. First, remove an adsorbed particle in the form of an atom. This step requires an amount of energy  $\varphi_a$ . Next, ionize

the atom in the vapor state. This requires an amount of energy  $V_{\rm f}$ . Finally, return the electron to the surface, thus obtaining an amount of energy equal to  $\varphi_{\rm e}$ . Therefore, the net amount of energy required to remove an ion from the surface is given by the standard expression:

$$\varphi_{\rm p} = \varphi_{\rm a} + V_{\rm f} - \varphi_{\rm e} \tag{13}$$

Since  $\varphi_a$  and  $\varphi_e$  have been calculated theoretically, it follows that  $\varphi_p$  is also known as a function of coverage and the material properties of the substrate-adsorbate system.

A typical schematic potential diagram indicating the relationship between  $\varphi_p$  and  $\varphi_a$  is shown in fig. 1. The adsorbed particle is located in the potential well of the energy diagram and requires an amount of energy  $\varphi_a$  or  $\varphi_p$  to be desorbed either as an atom or as an ion, respectively.



DISTANCE FROM SUBSTRATE NUCLEI

Fig. 1. Schematic potential energy diagram of an adsorbed metallic particle on a metallic surface showing the energy balance  $\varphi_p = \varphi_a - \varphi_e + V$  and the equilibrium double layer (dipole moment) thickness,  $R\cos\beta$ .

If desired, it is also a simple matter to calculate the energies required to remove adsorbed particles either in the form of free excited atoms or in the form of free excited ions. Evidently, these energies are greater than  $\varphi_a$ or  $\varphi_p$ , respectively, because of the additional excitation energy. Therefore, the desorption of excited species is less likely than that of the corresponding ground state species.

#### 2.4. Discussion of the physical constants appearing in $\varphi_a$ and $\varphi_p$

The physical constants of an adsorption system, necessary for the calculation of  $\varphi_a$  and  $\varphi_p$ , are the heats of desorption ( $\varphi'_m$ ,  $\varphi'_f$ ), the electron work

# ADSORPTION PHYSICS I

### TABLE 1A

Metal	φ <sub>m</sub> <sup>a</sup> Heat of sublimation (eV)	φm <sup>b</sup> Electron work function (eV)	rm <sup>c</sup> Covalent radius (Å)	S <sub>m</sub> <sup>d</sup> Orbital strength
Ti	4.84	(3.95)	1.32	2.62
v	5.33	(4.12)	1.22	2.62
Cr	4.11	4.60	1.17	2.31
Mn	2.89	(3.83)	1.17	2.62
Fe	4.32	(4.40)	1.16	2.62
Со	4.41	4.40	1.16	2.62
Ni	4.39	5.03	1.15	2.62
Zr	6.34	4.21	1.45	2.62
Nb	7.71	4.01	1.34	2.62
Мо	6.84	4.38 <sup>s</sup>	1.29	2.31
Tc	6.73	4.40 <sup>i</sup>	1.26	2.31
Ru	6.25	(4.52)	1.24	2.31
Rh	5.77	4.80	1.25	2.31
Pd	4.08	4.99	1.28	2.62
Hſ	7.29	(3.53)	1.44	2.62
Та	8.11	4.19	1.34	2.62
W	8.68	4.62 <sup>h</sup>	1.30	2.62
Re	8.07	5.10	1.28	2.62
Os	6.74	(4.55)	1.25	2.62
Ir	6.51	(5.30)	1.26	2.62
Pt	5.85	5.32	1.29	2.31

Physical	constants	of	transition	Metals
I IIYSICal	Constants	UI.	uansition	IVICIAIS

TABLE	1B
-------	----

Physical constants of metallic adsorbates

Film	φt' <sup>a</sup> Heat of sublima- tion (eV)	φ <sub>f</sub> <sup>b</sup> Electron work function (eV)	rt <sup>c</sup> Covalent radius Å	Sr <sup>d</sup> Orbital strength	α <sup>e</sup> Polariz- ability Å <sup>3</sup>	V <sub>f</sub> t Ioniza- tion potential (eV)	v Valence
Cs	0.80	1.81	2.35	1.00	13.0	3.87	1
Rb	0.84	2.09	2.16	1.00	10.1	4.16	1
Κ	0.92	2.24	2.02	1.00	8.2	4.32	1
Na	1.12	2.28	1.57	1.00	3.9	5.12	1
Li	1.66	2.49	1.22	1.00	1.8	5.36	1
Ba	1.80	2.48	1.98	1.29	12.8	5.19	2
Sr	1.69	2.74	1.91	1.29	11.5	5.67	2
Ca	1.82	2.71	1.74	1.29	8.7	6.09	2
Mg	1.54	3.68	1.37	1.29	4.2	7.61	2
Be	3.31	3.92	0.89	1.29	1.2	9.28	2
В	6.11	(4.5)	0.88	1.58	1.6	8.26	3
Al	3.35	4.08	1.25	1.58	4.5	5.96	3
Th	6.29 <sup>j</sup>	3.35	1.65	2.62	7.4	6.70	2

functions  $(\varphi_m, \varphi_f)$ , the angular strengths  $(S_f, S_m)$ , the covalent radii  $(r_m, r_f)$ , the valence (v) and the polarizability  $(\alpha)$  of the adsorbate and the surface density  $(\sigma_f)$  of the adsorbed particles at a coverage of one monolayer  $(\vartheta = 1)$ .

An approximate theoretical calculation of the polarizability is given in ref. 1. The values of  $\alpha$  and typical values of the other physical constants for 13 adsorbates and 21 substrate transition metals, taken from standard references, are tabulated in table 1. The constants can be used to calculate representative values of  $\varphi_a$  and  $\varphi_p$  for all combinations of these materials according to the formalism that is developed in this paper.

It must be emphasized that the typical physical constants in table 1 are not universal since most of them are sensitive to the crystallographic orientation of the substrate. To evaluate the dependence of the physical constants on the crystallographic structure is outside the scope of this work. It is recognized, however, that the constants merely enter the formalism as input parameters and can therefore be measured exprerimentally for a given crystallographic surface arrangement.

Since there is some divergence of opinion as to the proper experimental definition of  $\sigma_{\rm f}$ ,  $\varphi_{\rm f}$ , and  $\varphi_{\rm m}$ , the following prodecures are recommended which seem to be consistent with the proposed formalism. The density  $\sigma_{\rm f}$ can be experimentally defined as that adsorbate density where the desorption energy drops substantially from the high value of the first layer to the low value of the second layer. Experimental data<sup>3</sup>) and theoretical calculations, which will be presented in part II of this work, show that the transition is fairly sharp for metallic particles adsorbed on metals. The density  $\sigma_{\rm f}$  can be determined\* by using the techniques of Taylor and Langmuir or those of Moore and Allison. The electron work function  $\varphi_f$  can be experimentally defined as the effective work function (Richardson constant 120) at the point of determination of  $\sigma_f(\vartheta = 1)$ . For example,  $\varphi_f$  for cesium adsorbed on a metal is not always 1.81 eV; it may vary slightly, depending on the substrate crystallographic structure. Similarly,  $\varphi_m$  may be experimentally defined as the effective work function (Richardson constant 120) at  $\vartheta = 0$ . If the input parameters,  $\sigma_{\rm f}$ ,  $\varphi_{\rm f}$  and  $\varphi_{\rm m}$  are measured for a particular crystallographic surface, then they can be used in the theoretical equations, and the comparison of theory with experiment is most meaningful. Otherwise, typical values of these parameters (table 1) can be used as first approximations. Calculations show that the desorption energy  $\varphi_a$  is sensitive to the values of  $\varphi_m$  in the range  $0 < \vartheta < 0.5$ ; it is sensitive to  $\sigma_f$  in the range  $0.2 < \vartheta < 0.7$ , but it is relatively insensitive to  $\varphi_f$  over the entire range of coverage.

\* The substrate density  $\sigma_m$  can be deduced from  $\sigma_t$ , or vice versa, if the surface packing can be visualized in terms of simple geometric patterns (see also ref. 1).

Admittedly, there are other errors that are introduced in the formalism even when certain input constants are accurately measured experimentally. For example, the polarizability  $\alpha$  is not well known, the numerical values of the ratios between dipole moment and electronegativity (Pauling's ratio<sup>30</sup>) and work function and electronegativity (Gordy-Thomas ratio<sup>31</sup>) that were used in the derivation of  $\varphi_e$  and *F*, are not known with 100% accuracy, the orbital strengths cannot always be exactly calculated, etc. Assuming that the uncertainty is 20% in  $\alpha$ , 5% in the Pauling ratio, 3% in the Gordy-Thomas ratio and 1% for each of the quantities  $\varphi'_m$ ,  $\varphi'_f$ ,  $S_m$ ,  $S_f$ ,  $\vartheta_m$ ,  $\varphi_f$ , then for all coverages the uncertainty in  $\varphi_a$  is estimated to be of the order of 3%. In addition, the idealized pyramidal molecule<sup>1</sup>) used for calculating  $\varphi_e$  and *F*, and the idealized separation of  $\varphi_a$  into an ionic and covalent part, are extreme simplifications of the actual complicated physical system.

In spite of all the ambiguities and difficulties, the derived formalism seems to be in good agreement with experimental data as indicated by the detailed comparison between theory and experiment of the next section.

#### 3. Comparison of theory with reported experimental results

# 3.1. EXPERIMENTAL DATA FOR CESIUM ON TUNGSTEN

Desorption energies for cesium on tungsten have been studied experimentally by Taylor and Langmuir<sup>3</sup>) who report the following measured values for some of the constants of the system

$$\sigma_{\rm f} = 4.8 \times 10^{14} \,{\rm Cs} \,{\rm atoms/cm}^2$$
;  $\varphi_{\rm m} = 4.62 \,{\rm eV}$ ;  $\varphi_{\rm f} = 1.81 \,{\rm eV}^*$ 

These authors obtain the desorption energy  $\varphi_a$ , as a function of  $\vartheta$ , by measuring the atom emission rate  $E_a$  and using the experimental definition\*

$$\varphi_{a} = \frac{1}{5050} \frac{\partial \log E_{a}}{\partial (1/T)} \bigg|_{\vartheta = \text{constant}}$$
(14)

The reported results are shown in fig. 2 as circles.

The desorption energy  $\varphi_a$  can also be calculated by means of eq. (12.) In this equation, the particular reported experimental input values  $\sigma_f$ ,  $\varphi_m$ ,  $\varphi_f$  are used and the other necessary physical constants are taken from table 1. The results of the calculation are tabulated in table 2 and are superimposed

<sup>\*</sup>  $\varphi_{\rm f}$  was measured to be 1.81 eV at a coverage of many monolayers. Data, however, for  $\vartheta \leq 1$  indicated that  $\varphi_{\rm f} = 1.81$  eV for  $1 \leq \vartheta \leq \infty$ , for this particular system.

<sup>\*</sup> This relationship is also derived in part II from a rigorous statistical mechanics treatment of the composite surface.

#### TABLE 2

9	φ <sub>e</sub> (eV)	F	H <sub>ii</sub> (eV)	H <sub>ce</sub> (eV)	φ <sub>a</sub> (eV)	φ <sub>p</sub> (eV)
10-5	4.62	0.256	1.18	1.70	2.88	2.13
0.001	4.62	0.256	1.18	1.70	2.88	2.13
0.002	4.62	0.256	1.18	1.70	2.88	2.13
0.02	4.48	0.256	1.15	1.70	2.85	2.24
0.04	4.33	0.256	1.11	1.70	2.81	2.35
0.06	4.16	0.253	1.05	1.70	2.75	2.46
0.08	4.01	0.251	1.01	1.70	2.71	2.57
0.10	3.85	0.249	0.96	1.70	2.66	2.68
0.20	3.15	0.229	0.72	1.71	2.43	3.15
0.30	2.58	0.201	0.52	1.72	2.24	3.51
0.40	2.18	0.166	0.36	1.73	2.09	3.78
0.50	1.93	0.128	0.25	1.74	1.99	3.93
0.60	1.81	0.090	0.16	1.74	1.90	3.96
0.70	1.77	0.055	0.10	1.75	1.85	3.95
0.80	1.78	0.027	0.05	1.75	1.80	3.89
0.90	1.80	0.007	0.01	1.75	1.76	3.83
1.00	1.81	0.000	0.00	1.75	1.75	3.81
1.00+ to ∞	1.81	0.000	0.00	0.80	0.80	2.86

Calculated desorption energies for cesium adsorbed on a tungsten surface with  $\varphi_m = 4.62 \text{ eV } \varphi_t = 1.81 \text{ eV}$  and  $\sigma_t = 4.8 \times 10^{14} \text{ Cs atoms/cm}^2$ 



Fig. 2. Comparison of theoretical atom desorption energy  $\varphi_{a}$  for Cs on W (solid curve) with Taylor-Langmuir data (circles).  $\vartheta$  is the film coverage expressed in monolayers. The  $3^{0}/_{0}$  uncertainty limits are shown by the dashed lines, and the ionic and covalent contributions  $H_{11}$  and  $H_{cc}$  are also depicted. The dotted line for  $\vartheta \approx 1$  schematically represents  $\varphi_{a}$  when the second layer formation is taken into account.

on fig. 2 (solid line). The dashed lines on the figure indicate the 3% uncertainty limits of the calculation. Comparison of the experimental points with the theoretical calculation indicates very good agreement between theory and experiment over the entire range of coverage. Attempts of other authors to correlate the same data by semi-empirical correlation have not been successful<sup>32</sup>).

Inspection of the calculated curve indicates that the covalent contribution to the desorption energy is only weakly dependent on coverage while the ionic contribution is large at zero coverage and vanishes at a coverage of one monolayer. Also note that at low coverages the *change* of desorption energy,  $\Delta \varphi_a$ , is given by the approximate linear relation  $\Delta \varphi_a = F \Delta \varphi_e$ . Intuitively, Boudart<sup>33</sup>) has proposed a similar linear relationship between  $\Delta \varphi_a$  and  $\Delta \varphi_e$ .

The abrupt change in the desorption energy at  $\vartheta = 1$  is introduced by simply equating the index m to the index f in eq. (12) since at this point the adsorbate particles are adsorbed on similar adsorbate particles. This rather abrupt change is also present in the Taylor and Langmuir data (fig. 27, p. 454 of reference 3). Admittedly, the analytical discontinuity at  $\vartheta = 1$  is somewhat artificial and in actual fact it should be replaced by a steep but continuously varying (and temperature dependent) curve, as schematically indicated by the dotted line of fig. 2. The continuous transition is due to the physical fact that the second layer starts building up before the first layer is completed. This fact is not reflected in eq. (12). An approximate analysis of the phenomenon, however, is given in part II of the present work.

Taylor and Langmuir do not measure  $\varphi_p$  directly because of experimental difficulties. Instead, they calculate  $\varphi_p$  from eq. (13) by using experimentally determined values of  $\varphi_e$  and  $\varphi_a$ . Since it has already been shown that the theoretical values of  $\varphi_e$  and  $\varphi_a$  are in good agreement with experiment, no new information is gained by further comparison of theoretical and reported values of  $\varphi_p$ .

If desired, similar coverage dependent calculations for  $\varphi_a$  and  $\varphi_p$  for other adsorption systems, besides cesium and tungsten, can be derived. Unfortunately, there is no other reliable experimental data to check these calculations. The reason is that other experimenters who report values of  $\varphi_a$ versus  $\vartheta$ , measure  $\vartheta$  relatively and not absolutely; they do not specify  $\sigma_f$ ,  $\varphi_m$ and  $\varphi_f$  of the investigated surface; nor do they define  $\varphi_a$  according to eq. (14). Hence any comparisons would be somewhat ambiguous.

# 3.2. EXPERIMENTAL DATA ON INITIAL DESORPTION ENERGIES FOR DIFFERENT ADSORBATES ON TUNGSTEN

Initial desorption energies,  $\varphi_{a0}$ , of atoms at zero coverage, for a variety

of adsorbates on tungsten, have been reported by many experimenters<sup>2-4</sup>, <sup>8,10,17,18,34-38</sup>). These results are shown by the crosses of fig. 3. Unfortunately, few of these workers specify  $\varphi_m$  and  $\varphi_f$  ( $\sigma_f$  does not appear in  $\varphi_{a0}$ ), and even fewer experimentally determine  $\varphi_{a0}$  from the correct definition given by eq. (14). A critique of some of the inaccurate theories used to determine  $\varphi_{a0}$  is given in part II.

For lack of better information, corresponding desorption energies are calculated by means of eq. (12) using the *typical* values of the physical constants given in table 1. When  $\varphi_{p0}$  is reported, eq. (13) is used in addition



Fig. 3. Comparison of theoretical values of  $\phi_{a0}$  (circles) with experimental values (crosses) for various metals adsorbed on tungsten at zero coverage.

to obtain  $\varphi_{a0}$ . The theoretical results are superimposed on fig. 3 (circles).

A comparison of theory and "experiment" shows a fair numerical agreement and the proper trends among the alkalis and the alkaline earths. The unusual dip of  $\varphi_{a0}$  for Mg is obtained from theory because Mg has an exceptionally low heat of sublimation compared to its neighbors Ca and Be. It is significant that the same dip has also been observed experimentally by Zingerman<sup>39</sup>). Also, the theory correctly predicts the relatively high desorption energy for Th on W.

Many discrepancies exist between different experimental values of  $\varphi_{a0}$  reported for a given adsorption system. For example, Bosworth<sup>35</sup>) reports an unusually low value ( $\varphi_{a0} = 1.4 \text{ eV}$ ) for Na on W. This value is about  $\frac{1}{2}$  of that reported more recently<sup>34</sup>). This huge difference may be due to surface contamination or may be due to the questionable cross-plotting and compensating of raw data used by Bosworth. Also, an experimenter carrying out experiments on supposedly similar substrate surfaces, may find different values of  $\varphi_{a0}$ , presumably due to alterations in crystallographic structure. For example, Moore and Allison<sup>2</sup>) report  $\varphi_{a0}$  values differing by about 5% for Sr on W.

In summary, surface contamination, questionable procedures used in processing experimental data, and differences in crystallographic structure of the surface are probably the main causes for disagreement among various experimental values, and between these values and theoretically calculated values of  $\varphi_{a0}$ .

### 3.3 OTHER EXPERIMENTAL DATA

Zingerman *et al.*<sup>39</sup>) measure  $\varphi_a$  as a function of the number of adsorbed particles for the system of Ba on polycrystalline W. They find that  $\varphi_a$  falls linearly with coverage until a coverage of about  $7 \times 10^{14}$  atom/cm<sup>2</sup> is reached, whereby  $\varphi_a$  sharply reduces to a value near the heat of sublimation of bulk Ba. In a later work<sup>4</sup>) the same authors measure  $\varphi_a$  for Ba, Sr, Ca, Mg and Be on W as a function of the number of adsorbed particles and they report that the full coverage density is less than  $6 \times 10^{14}$  atoms/cm<sup>2</sup>. They qualitatively find that the roughly linear decrease in  $\varphi_a$  from low to high coverage is about 1 eV for Ba, Sr, Ca and Mg and is about  $\frac{1}{2}$  eV for Be. Similar experimental results are obtained<sup>40</sup>) for Ba on a tungsten single crystal, even though there is evidence of surface contamination<sup>4, 41</sup>). All of the above results are in qualitative agreement with eq. (12). More quantitative comparisons cannot be made, however, because these workers do not determine  $\varphi_a$  by means of eq. (14). A discussion of the procedures used by these workers to obtain  $\varphi_a$  is given in part II.

Recently  $\varphi_{p0}$  was measured for cesium and barium adsorbed on polycrystalline rhenium<sup>42</sup>). The reported values are Cs on Re:  $\varphi_{p0} = 2.01$  eV.; Ba on Re:  $\varphi_{p0} = 4.71$  eV. No other physical constants are given.

Using typical constants from table 1, the calculated values for the initial desorption energies of ions are Cs on Re:  $\varphi_{p0} = 1.93$  eV.; Ba on Re:  $\varphi_{p0} = 4.19$  eV. The agreement between the theoretical and the experimental values can be considered as good in view of the uncertainties of the input data used in the calculation with respect to the conditions prevailing in the experiment.

# 3.4. CALCULATION OF INITIAL DESORPTION ENERGIES FOR CESIUM ON TRAN-SITION METALS

Cesium is used in thermionic energy converters because it promotes electron and ion emission when it is adsorbed on the electrodes of the converter. The electrodes are usually transition metals. It is interesting to calculate the initial desorption energies  $\varphi_{a0}$  and  $\varphi_{p0}$  for cesium on different transition metals because these energies are indicative of the relative suitability of these materials as electrodes.

Using the typical values of table 1,  $\varphi_{a0}$  and  $\varphi_{p0}$  for cesium on 21 transition

Т	ABLE	3
1	ABLC	୍ତ

Metal	Atomic number	φ <sub>a0</sub> (eV)	$\varphi_{p0}$ (eV)	$\chi_0 = \varphi_{a0}/\varphi_{m}$	φm (eV)
Ti	22	2.05	1.97	0.520	3.95
V	23	2.23	1.98	0.541	4.12
Cr	24	2.47	1.74	0.537	4.60
Mn	25	1.71	1.75	0.446	3.83
Fe	26	2.26	1.73	0.514	4.40
Co	27	2.26	1.73	0.514	4.40
Ni	28	2.72	1.56	0.540	5.03
Zr	40	2.38	2.04	0.565	4.21
Nb	41	2.42	2.28	0.603	4.01
Мо	42	2.70	2.19	0.616	4.38
Тс	43	2.69	2.16	0.612	4.40
Ru	44	2.71	2.06	0.600	4.52
Rh	45	2.83	1.90	0.590	4.80
Pd	46	2.62	1.50	0.525	4.99
Hf	72	2.14	2.48	0.606	3.53
Та	73	2.58	2.26	0.616	4.19
W	74	2.88	2.13	0.624	4.62
Re	75	3.16	1.93	0.620	5.10
Os	76	2.68	2.00	0.590	4.55
Ir	77	3.15	1.72	0,594	5.30
Pt	78	3.21	1.76	0,603	5.32

Theoretical values of  $\varphi_{a0}$ ,  $\varphi_{p0}$  and  $\chi_0$  calculated for C<sub>s</sub> on 21 transition metals.  $\varphi_m$  is shown for comparison with  $\varphi_{a0}$ 

metals are calculated by means of eqs. (12) and (13) and are tabulated in table 3. The bare electron work function  $\varphi_m$  of these transition metals is also reproduced in the same table. Inspection of the results reveals certain interesting features.

The initial desorption energy for the different transition metals lies in the range of 2-3 eV. In decreasing order of  $\varphi_{a0}$ , the metals considered can be arranged as: Pt, Re, Ir, W, Rh, Ni, Ru, Mo, Tc, Os, Pd, Ta, Cr, Nb, Zr, Fe, Co, V, Hf, Ti and Mn.

The ratio  $\chi_0 = \varphi_{a0}/\varphi_m$  is practically the same for all the transition metals. In other words, the metals that have high binding energies for adsorbed electropositive atoms also have high binding energies (work function) for electrons. This general trend has already been suspected and observed by several workers<sup>11, 43, 44</sup>) and gives somewhat further support to the theoretical equation for  $\varphi_a$ . In part III the same parameter  $\chi_0$  appears again in an approximate optimization study of electron emitting materials. The comparison of the results of part III with experiment are consistent with the constancy of  $\chi_0$ .

The desorption energy  $\varphi_{p0}$  for ions is in the range of 1.5–2.5 eV for most of the transition metals but it is not simply correlated with  $\varphi_{a0}$  or  $\varphi_{m}$ .

In order of decreasing  $\varphi_{p0}$  the metals considered are arranged as: Hf, Nb, Ta, Mo, Tc, W, Ru, Zt, Os, Ti, V, Re, Rh, Pt, Ir, Mn, Cr, Fe, Co, Ni and Pd. A good ion emitter is characterized by a high  $\varphi_{a0}$  and low  $\varphi_{p0}$ . In this respect most of the transition metals satisfy this requirement for zero or very small coverage.

#### 4. Conclusions

By extension of the concepts of molecular chemical bonds to metallic particles adsorbed on metallic surfaces, it is possible to calculate the energies required for the desorption of atoms and ions from the corresponding composite surfaces. The derived correlations give these energies as functions of the degree of coverage and material and crystallographic properties of the substrate and adsorbate. The calculations do not involve any arbitrarily adjustable constants. Their range of applicability extends to all degrees of coverage  $(0 < \vartheta < \infty)$  and to all intermetallic adsorption systems that involve monatomic adsorbates.

The agreement between theoretical predictions and experimental results is very good, whenever meaningful comparisons can be made, and indicative of well established general trends in other cases where the experimental results have been inadequately reported.

This study and the previous electron work function study<sup>1</sup>) mutually reinforce each other, since they are both based on similar extensions of molecular physics to adsorption physics.

The theoretical calculation of  $\varphi_e$  and F, and consequently of the desorption energies, presumes a homogeneous surface<sup>1</sup>). Therefore, no surface patch effects are included in the calculations proposed in this paper. It is felt, however, that this is not a drawback of the theory because, if a distribution of patches is established, then the theory can be applied to each homogeneous patch individually.

The theory does not include the small but complicating effects of thermal expansions which would cause  $\varphi_a$  and  $\varphi_p$  to be slightly dependent on the surface temperature. Finally, the analysis does not apply to impregnated cathodes, such as the L cathodes, because the surface is not pure, and it does not apply to unusual but likely cases of adsorbed metallic particles burrowing under the surface or spontaneously clustering at coverages less than one monolayer. These phenomena have been observed for certain gases on metals<sup>45</sup>) and on semiconductors<sup>46</sup>).

It is felt that a similar extension of molecular concepts to surface physics will bear fruitful results even in the more complicated case of adsorption of non-metallic particles, such as hydrogen, oxygen, etc., on metals. This topic will be discussed in a future communication.

#### Appendix

#### Determination of the orbital strength S for metals

Hultgren<sup>29</sup>) proves a general theorem concerning S values. The theorem states that the best bond orbital that can be found by hybridization of pure atomic orbitals, consisting of one or more complete subshells, has a strength equal to the square root of the number of orbitals. For example,  $S = \sqrt{1}$  for s-orbitals,  $\sqrt{3}$  for p-orbitals,  $\sqrt{5}$  for d-orbitals,  $\sqrt{4}$  for sp<sup>3</sup>-orbitals, and  $\sqrt{9}$  for sp<sup>3</sup>d<sup>5</sup>-orbitals. The question then is "how does one assign S-values to the elements of the adsorption system of interest to this paper?" This question can be answered by three different methods.

a) assign S values characteristic of the elements in their atomic vapor state,

b) assign S values characteristic of the elements in their combined states,

c) assign S values taken from the arithmetic mean of methods (a) and (b). For lack of definite criteria, the third intermediate alternative is chosen and thus the S-values for the different metal elements can be derived as follows.

Alkali group (Cs, Rb, K, Na and Li). These elements in the vapor state have spherically symmetric s-orbitals, so according to method (a) S = 1. In a lattice, the alkali elements are also presumed to have spherically symmetric orbitals, because Seitz<sup>47</sup>) obtains accurate cohesive energies for the alkali crystals using wave functions differing little from the atomic wave functions. Therefore, S is again equal to unity for combined states and according to method (c) the S-value for this group is unity.

Tetravalent elements (Be, C, Si and Ge). These elements in the vapor state have two paired s-electrons and two unpaired p-electrons, so according to method (a)  $S = \sqrt{3}$ . In the combined state, however, four equivalent tetrahedral orbitals frequently form and Pauling<sup>28</sup>) shows that these arise naturally from sp<sup>3</sup>-hybrids. Thus, according to method (b), S = 2. Finally, according to method (c), the S-value for the group is  $S = \frac{1}{2}(\sqrt{3} + 2) =$ 1.87, not differing greatly from that of methods (a) or (b).

Divalent elements (Ba, Sr, Ca, Mg and Be) and trivalent elements (Tl, In, Ga, Al and B). These elements are much more difficult to evaluate because they do not have well defined S values in the metallic combined states. Nevertheless, if it is assumed that the S values of elements with valences 1, 2, 3, 4 have the relative ratios 1:2:3:4, then the S value of divalent elements becomes 1.29 and the S value for trivalent elements becomes 1.58.

Transition elements. These elements are even more difficult to treat. In the vapor state the transition metals fall into two subgroups. The elements of subgroup 1 (Ti, V, Mn, Fe, Co, Ni, Zr, Pd, Hf, Ta, W, Re, Os and Ir)

contain two paired s-electrons or no s-electrons and unpaired d-electrons. Hence, according to method (a),  $S = \sqrt{5}$ . The elements of subgroup 2 (Cr, Mo, Tc, Ru, Pt and Rh) contain an unpaired s-electron in addition to unpaired d-electrons. Thus, method (a) applied to this subgroup gives the slightly different approximate result  $S = \frac{1}{2}(\sqrt{5} + 1)$ . In the combined state all the transition elements enter into s, p, and d-hybridizations, where the maximum possible strength is just 3. Thus, according to method (b), S = 3.

Therefore, according to method (c), the S values for transition elements are:  $S = \frac{1}{2}(\sqrt{5} + 3) = 2.62$  for subgroup 1, and  $S = \frac{1}{2}(1.63 + 3)/2 = 2.31$  for subgroup 2.

*Thorium*. This element is a member of the actinide series, but in fact it is chemically similar to hafnium, having two paired s-electrons and unpaired d-electrons. Thus, it can be included in subgroup 1 of the transition metals mentioned above.

The transition metal Nb is an unusual case. According to tables of atomic structure Nb should belong to subgroup 2, but according to Latimer and Hildebrand <sup>48</sup>), Nb should belong to subgroup 1. The latter choice for S results also in better agreement between calculated and experimental values of  $\varphi_{a0}$  as inferred from electron emission data in part III.

The results of this discussion are tabulated in table 1.

a)  $\varphi'$  is obtained from Sanderson's enthalpy values (R. T. Sanderson, *Chemical Periodicity*, Reinhold Publ. Co., N.Y. 1960) p. 72 by the theoretical relation  $\varphi' = H - \frac{1}{2}kT$  (room) except where otherwise noted.  $\frac{1}{2}kT$  (room) is only 0.013 eV. Various authors differ somewhat in their quoted values, but Sanderson's compilation is fairly up-to-date (1960) and covers all the elements of interest except thorium.

b)  $\varphi_m$  is obtained from *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Co., Cleveland, 42nd edition 1961) p. 2594, except where otherwise noted. Unbracketed values are those preferred by Michaelson for typical polycrystalline surfaces. Bracketed values are those for which Michaelson gives no preference because of considerable uncertainty. Michaelson also does not indicate which values are effective electron work functions (Richardson constant = 120).

c) A. R. Von Hippel, *Molecular Science and Engineering*, (John Wiley and Sons, N.Y. (1959) p. 148.

d) Calculated by the procedure outlined in the appendix.

e) Calculated as indicated in ref. 1.

f) Handbook of Chemistry and Physics, (1961), p. 2586.

g) For Mo,  $\varphi_m = 4.38$  eV as recently reported by R. L. Amodt, L. J. Brown and B. D. Nichols, J. Appl. Phys. 33 (1962) 2080.

h) For W,  $\varphi_m = 4.62$  eV as reported both by J. B. Taylor and I. Langmuir<sup>3</sup>), and recently by J. M. Houston in "Proc. Round Table Discussion on Cathode Emission", (Power Information Center, Univ. of Penn. 1961).

i) For Tc,  $\phi_m$  is not reported at all. Value is predicted by H. B. Michaelson, J. Appl. Phys. 21 (1950) 536.

j) For Th,  $\varphi_1'$  is not reported by Sanderson, so it is taken from C. J. Smithells *Metals* Reference Book Vol. II (Buttersworth Publ. London, 2nd ed., 1955) p. 575.

k) For Th,  $V_t$  is not reported anywhere. Value is chosen from the approximate relation  $V_t = 2\varphi_t$ .

#### References

- 1) E. P. Gyftopoulos and J. D. Levine, J. Appl. Phys. 33 (1962) 67.
- 2) G. E. Moore and H. W. Allison, J. Chem. Phys. 23 (1955) 1609.
- 3) J. B. Taylor and I. Langmuir, Phys. Rev. 44 (1933) 423.
- 4) Ya. P. Zingerman, V. A. Ishchuk and V. A. Morozowski, Soviet Physics-Solid State, 3 (1961) 760.
- 5) W. Shockley, Phys. Rev. 56 (1939) 317.
- 6) T. B. Grimley, Advances in Catalysis XII (Academic Press, N.Y., 1960) p. 1;
   J. Phys. Chem. Solids 14 (1960) 227.
- 7) J. Koutecky, Trans. Faraday Soc. 54 (1958) 1038; J. Phys. Chem. Solids, 14 (1960) 233.
- 8) J. Becker, Advances in Catalysis VII (Academic Press, N.Y., 1955) p. 135.
- 9) B. M. W. Trapnell, Chemisorption (Butterworths Publ., London, 1957) p. 147.
- F. L. Hughes, Phys. Rev. 113 (1959) 1036;
   F. L. Hughes and H. Levinstein, Phys. Rev. 113 (1959) 1029.
- N. S. Rasor and C. Warner III, Atomics International First Summary Report of Basic Research in Thermionic Energy Conversion Processes, (Nov. 1961).
- 12) R. W. Gurney, Phys. Rev. 47 (1935) 479.
- 13) J. C. Slater, *Quantum Theory of Matter* (McGraw-Hill Book Company, N.Y., 1951) p. 283.
- 14) D. D. Eley, Disc. Faraday Soc. 8 (1950) 34.
- 15) D. P. Stevenson, J. Chem. Phys. 23 (1955) 203.
- 16) J. H. de Boer, Advances in Catalysis VIII (Academic Press, N.Y., 1956) p. 123.
- 17) W. E. Danforth, J. Appl. Phys. 33 (1962) 1972.
- 18) E. Ya. Zandberg, Soviet Physics 5 (1961) 186.
- 19) V. M. Gavriluk, Ukrains'kyi Fizichnyi Zhurnal 4 (1959) 734.
- 20) I. Higuchi, T. Ree and H. Eyring, J. Amer. Chem. Soc. 77 (1955) 4969 and 79 (1957) 1330.
- 21) L. Pauling *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, N.Y., 3rd. rev. ed., 1960).
- 22) J. C. Slater, Quantum Theory of Matter (McGraw-Hill, N.Y., 1951) p. 231.
- 23) I. T. Wall, J. Amer. Chem. Soc. 61 (1939) 1051.
- 24) T. Ri and N. Muroyama, Proc. Imperial Academy of Japan 20 (1944) 93.
- 25) C. A. Coulson, Valence (Oxford Univ. Press, London, 2nd rev. ed., 1961) p. 128.
- 26) H. C. Gatos and A. J. Rosenberg, *The Physics and Chemistry of Ceramics*, C. Klingsberg, Ed. (Science Publishers, Inc., New York).
- 27) Ref. 25, p. 125.
- 28) Ref. 21, p. 108.
  L. Pauling, J. Amer. Chem. Soc. 53 (1931) 1367.
  L. Pauling and J. Sherman, J. Amer. Chem. Soc. 59 (1937) 1450.
- 29) R. Hultgren, Phys. Rev. 40 (1932) 891.
- 30) Ref. 21., (2nd ed. 1944) p. 86.
- 31) W. Gordy and W. Thomas, J. Chem. Phys. 24 (1956) 439.
- 32) J. H. de Boer, Chemisorption W. E. Garner Ed. (Academic Press, N.Y., 1957) p. 31.
- 33) M. Boudart, J. Amer. Chem. Soc., 72 (1952) 3556.
- 34) S. V. Stardubtsev, Zhurnal Eksp. i Teor, Fiz. 19 (1949) 215.
- 35) R. C. L. Bosworth, Proc. Roy. Soc. A162 (1937) 323.
- 36) A. M. Romanov, Soviet Physics Technical Physics 2 (1958) 1125.
- 37) F. Knauer, Z. Physik 125 (1948) 278.
- 38) M. D. Scheer and J. Fine, J. Chem. Phys. 37 (1962) 107.
- 39) Ya. P. Zingerman, V. A. Ishchuk and V. A. Morozowski, Soviet Physics Solid State 3 (1961) 2030.
- 40) V. M. Gavriluk and V. K. Medvedev, Soviet Physics Solid State 4 (1963) 1737.
- 41) Ya. P. Zingerman and V. A. Ishchuk, Soviet Physics Solid State 4 (1963) 1618,
- 42) M. D. Scheer and J. Fine, J. Chem. Phys. 38 (1963) 307,

- 43) Ref. 16, p. 112.
- 44) S. T. Martin, Phys. Rev. 56 (1939) 947.
- 45) Ref. 16, p. 92, 104.
- 46) J. J. Lander and J. Morrison, J. Appl. Phys. 34 (1963) 1411.
- 47) F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940) p. 348.
- 48) W. M. Latimer and J. H. Hildebrand, *Reference Book of Inorganic Chemistry* (Macmillian Co., N.Y., 3rd edition 1951) p. 357.