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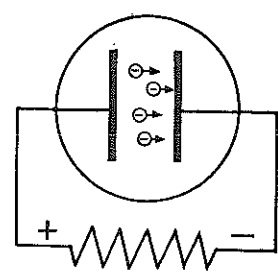
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COMMENTS ON
WORK FUNCTION THEORIES*

by

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INTRODUCTION

The emission properties of the surfaces of the electrodes of a thermionic converter play the most important role in the determination of the optimum performance characteristics of the converter. Future advances in converter performance may well be achieved by means of better electrode surfaces. This point is illustrated by the substantial experimental effort which presently is devoted to the study of surface properties. An example of such a property is the work function. The value of the work function depends on the material, the crystallographic orientation of the surface, the degree to which the surface is covered by adsorbates, and the temperature of the surface.

The theoretical understanding of surface properties is not as advanced as it might be. Although many practical results have been obtained, there is still a lot of work which needs to be done.

The purpose of this paper is to discuss briefly some of the theoretical work which has been done about surface properties, with emphasis on the work function of electrodes for thermionic converters only. The paper is not meant to be an exhaustive or even adequate review of the literature on the subject. It attempts to focus attention on a few points only.

* Invited paper.

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The paper is organized as follows. First, the definition of the work function ϕ is given. Although this definition is well known, it is repeated here in order to focus attention on the importance of the points just outside the surface and on the requirements for a rigorous calculation of the work function. Second, the information needed for the calculation of ϕ is discussed. This information is not available and very likely will not become available for many years to come. Third, theoretical analyses of bare work functions are briefly reviewed.

From the review of the limited number of approximate calculations
which have been performed it is concluded that the understanding of surface phenomena is neither complete nor accurate. From the review of the semi-empirical correlations it is concluded that only one of these correlations attempts to account for the dependence of ϕ on crystallographic orientation. Fourth, analyses of work functions of composite surfaces are briefly summarized. From the summary of some approximate calculations it is seen that work in this area is minimal and inconclusive. From the summary of the two semi-empirical correlations used in the field of thermionic conversion it is concluded that both correlations yield practical numerical results but that no particular fundamental significance can be assigned to the models used for their derivation.

DEFINITION OF WORK FUNCTION

Given a surface of a crystal lattice, the work function ϕ of the surface is defined as the reversible work per electron required to take an infinitesimal charge in equilibrium with the electrically neutral lattice to a state of zero entropy and zero energy at a point just outside the surface. This is also the definition of the negative of the value of

the chemical potential of the points just outside, or the negative of the value of the electrochemical potential with respect to the points just outside. Work function is, in general, a function of the temperature of the surface.

It must be noted that ϕ can be regarded as a meaningful property of a surface only with respect to the points just outside. These points are about 500 Å from the plane of the surface lattice-sites. Operationally, they are defined as the points at which the value of the image force experienced by an electron escaping from the surface (the value of the correlation force) equals that of the force due to the space charge, in an arrangement in which the crystal and the adjacent electron gas phase are in thermodynamic equilibrium. Such an arrangement may be a thermionic converter with identical electrode surfaces, kept at the same temperature. The equality of the two types of forces means the following. Beyond the points just outside, the change in the potential energy of the image force is negligibly small while that of the space charge may be appreciable. On the other hand, before the points just outside, the change in the potential energy of the image and other interfacial forces is abrupt while space charge effects are completely negligible.

Without the concept of the points just outside, all surfaces of a given material would have either the same value of work function, independent of crystallographic orientation, or values of work function which depend on the magnitude of the space charge effects.

Experimentally, an apparent or Richardson work function ϕ^* is deduced from Schottky plots at different temperatures, extrapolated to zero field conditions. Implicit in this measurement of ϕ^* is the

assumption that ϕ is approximately a linear function of temperature. It can be readily shown that this assumption is equivalent to saying that the value of the apparent work function equals that of ϕ at zero degrees Kelvin.

More often than not, it is difficult to associate an accurate experimental value with the work function of a surface. The reason is not only because of errors in the experimental procedure but primarily because it is difficult to establish the nature of the surface with regard to either crystallographic orientation, or degree of contamination, or both.

INFORMATION NEEDED FOR THE CALCULATION OF ϕ

The rigorous calculation of the work function ϕ of a surface of a metal would require knowledge of the energy eigenvalues of the crystal regarded as an open thermodynamic system, namely the eigenvalues for all possible degrees of charging. In other words, given a piece of metal, complete sets of energy eigenvalues must be found for the metal being electrically neutral, being charged by one, two, . . . positive units of charge, and being charged by one, two, . . . negative units of charge. These sets of eigenvalues can be used in a well specified formalism, namely the formalism of grand canonical ensembles, to compute the electrochemical potential of the neutral metal.¹ If the arbitrary zero energy reference level is taken at the points just outside the surface, the negative of this electrochemical potential will be equal to ϕ^{\ddagger} . For an example of such a calculation of the electrochemical potential of an atom with Z electrons see reference 2. The procedure for the calculation of ϕ would be the same as that in reference 2, except that the energy eigenvalues would be those of the metal.

[‡] Thermodynamically, the value of the work function at zero temperature can be defined only as a limit of the value of ϕ as the temperature T approaches zero from positive values of T.

It is clear that the above rigorous approach to the calculation of ϕ is presently impossible and, therefore, drastic approximations are necessary. Nevertheless, knowledge of the exact procedure provides a useful reference for the interpretation of the various approximations that might be used in practice.

BARE WORK FUNCTIONS

Approximate Calculations. For the calculation of the work function of a surface of a pure metal, of the so-called bare work function, the following approximate procedure has been used. First, the calculation is restricted to that of the value ϕ^* of ϕ at zero temperature. Attempts are subsequently made to estimate an approximate temperature coefficient of ϕ .³ Second, the motions of the ion cores of the crystal are neglected. In other words, the Born-Oppenheimer approximation is used for the quantum-mechanical operator of the crystal. This approximation results in a many-electron problem. Third, the many-electron problem is approximated by an one-electron problem. The one-electron eigenvalue problem is solved and the interfacial electron motive corresponding to the ground state of the electronic structure is computed. In the context of the one-electron approximation, the value of ϕ^* is given by the difference between the values ψ_1 of the motive of the points just outside the metal surface and μ_F of the Fermi energy. The Fermi energy is taken either as that of the free-electron model or as that of some band structure calculation.

The interfacial motive is found to be the sum of three terms. One term is purely electrostatic and is due to the asymmetric charge distribution at the surface. This term is called the dipole moment effect. Another term accounts for the fact that an electron does not

act on itself. It is called the exchange effect (or exchange correction). Finally, the third term accounts for the fact that the presence of one electron at a particular position alters the distribution of and, hence, the potential energy due to the other charges. The third term is called the correlation effect. The three effects are not independent of each other but very closely interrelated.

Approximate calculations of the type discussed above have been made by several authors.⁴⁻⁷ Because of numerical difficulties, only monovalent metals are treated, and the crystallographic orientation of the surface is not considered explicitly (i. e. , all interfacial phenomena are analyzed as one-dimensional). The results are qualitatively similar and suggest the following conclusions.⁴

(a) The interfacial motive is largely due to exchange and correlation effects rather than ordinary electrostatic effects. A similar conclusion applies to ϕ^* .

(b) There is no single interfacial motive which is satisfactory for electrons of all velocities. Each electron, so to speak, has its own motive.

(c) The dipole moment effect is relatively small for monovalent metals.

Although these conclusions are informative, their generality is questionable. For example, it is generally accepted that exchange and correlation effects are important in determining both the electronic structure and the interfacial electron motive of a metal. As discussed by Slater,⁸ however, the dependence of these effects on electron velocity (conclusion (b) above) is a consequence of the approximations

introduced in the calculations rather than a representation of a true physical phenomenon.

With regard to the dipole moment effect, the situation is even more ambiguous. For monovalent metals, conclusion (c) cannot be judged because the accuracy of the expressions used for exchange and correlation effects is not known. For multivalent elements, many authors believe that the dipole moment effect is larger than that for monovalent elements. In fact, it is often stated that differences in the values of work functions of surfaces of the same metal but of different crystallographic orientations are due only to differences in the magnitude of the dipole moment effect.⁹⁻¹⁰ This statement cannot be correct. Exchange and correlation effects may be substantially different for different surfaces of the same element and, hence, may be partly the cause of the differences in work functions. Moreover, it may be argued that since the dipole moment effect is closely inter-related to the other effects, if the dipole moment effect changes the other effects must also change. It appears that no general conclusions can be stated until surface exchange and correlation effects are analyzed more accurately and by means of three-dimensional models, namely models which account explicitly for the crystallographic orientation of the surface.

The thermodynamic proof that "the difference in work functions of two surfaces of the same metal is due to dipole moment effects"¹⁰ is not correct. The reason is as follows. Essential to the proof in reference 10 is the assumption that the average electrostatic potential ψ_0 in the metal is uniform. The value of the average potential, however, depends on the direction along which the averaging is performed and, therefore, this value is different for directions normal to surfaces of

(a) The substrate material has a fixed electronic structure, namely a structure independent of the presence of adsorbate particles on the surface.

(b) For the substrate-adsorbate interactions, the surface of the substrate can be regarded as that of a perfect conductor.

(c) The adsorbate particles exist on the surface of the perfect conductor in two distinct energy eigenstates, one ionized and one neutral. The energy difference between these two states equals E . This energy can assume both positive and negative values.

(d) The relative degrees of coverage, Θ_i of the ionic state and Θ_a of the neutral state, are given by the Boltzmann relation

$$\Theta_a / \Theta_i = 2 \exp (-E/kT),$$

where T is the surface temperature. The degree of coverage Θ of the surface by the adsorbate particles equals the sum of Θ_i and Θ_a .

(e) The ion core is at a distance r_i from the surface, where r_i is the effective ionic radius of the adsorbate. This core is held on the surface by the image force.

(f) The ions and their image charges form a double layer on the surface, an array of dipoles on the surface. The potential drop across the double layer yields the change $\Delta\phi$ of the work function of the substrate.

By virtue of these assumptions plus considerations regarding depolarization effects and energy balances, Rasor and Warner obtain their correlation for $\Delta\phi$. This correlation may be expressed either as a function, $\Delta\phi(\Theta, T)$, of the coverage Θ and the temperature T , or,

(h) The overlap charge is proportional to a Morse function for Θ greater than about 0.3, and a modified Morse function for Θ smaller than about 0.3. The modified Morse function versus Θ has a slope different than zero at Θ equals zero in contrast to the Morse function versus Θ which has a slope equal to zero at Θ equals zero.

(i) The neutral orbital electronegativity at a coverage of one monolayer equals that of a pure adsorbate surface with the same particle arrangement. This is equivalent to saying that the work function of the composite surface at a coverage of one monolayer equals that of the pure adsorbate surface with the same particle arrangement.

By virtue of these assumptions plus considerations of depolarization effects, Gyftopoulos and Steiner obtain a correlation for $\Delta\phi$ versus Θ only, as well as a correlation for the desorption energy of the adsorbate versus Θ only. These correlations are then combined with the statistical analyses of Levine and Gyftopoulos^{22, 23} to find that, under certain conditions, the change $\Delta\phi$ in work function depends on T/T_R only.

For the correlation $\Delta\phi(\Theta)$ the following information is needed: the surface densities σ_s for the substrate and σ_f for the adsorbate, the atomic radii of the substrate and the adsorbate, the crystallographic orientation of the substrate surface, the polarizabilities of the substrate and adsorbate atoms, the valence of the adsorbate, the work functions ϕ_s at zero coverage and ϕ_f at full coverage, the energy D_o of the purely covalent substrate-adsorbate bond, and the sum of the differences of the ionization energy and electron affinity of the substrate and the adsorbate. The energy D_o is related to the heats of sublimation

of the substrate and the adsorbate.²⁴ For the correlation $\Delta\phi(T/T_R)$ the information required is the same as that for $\Delta\phi(\Theta)$.

This completes the discussion of the major assumptions and input information required for the correlations by Rasor and Warner, and by Gyftopoulos and Steiner. The assumptions and information needed are illustrative of the differences and similarities between the two correlations. Numerically, both correlations yield reasonable practical results for a variety of bimetallic systems, and have been found useful tools for the representation of data obtained from thermionic converters.

It should be noted that in spite of the numerical success of the correlations, no fundamental significance can be assigned to the models used for the calculation of the perturbation. What is meant by this observation is that no experiment can be devised which would conclusively indicate that the adsorbate particles exist on the surface as suggested by the models of either of the correlations.

In attempting to evaluate the practicality of these two correlations or any other correlation, a fruitful approach might be to check experimentally their internal consistency. Some questions which might be asked along this approach are as follows:

- (a) For a given Θ , does $\Delta\phi$ depend on T ?
- (b) Is the work function at a coverage of one monolayer primarily controlled by the adsorbate?
- (c) In fitting experimental data, are the resulting values of the input information consistent with the values that are expected from the definitions of these quantities?

(d) For a given adsorbate, does $\Delta\phi(T/T_R)$ depend only on the bare work function? etc.

Presently, the available experimental information is neither sufficiently accurate nor does it cover a sufficiently large range of surface conditions to allow conclusive answers to some of these questions. It is hoped that such information will become available in the future.

There are other important aspects of composite surfaces, such as the problem of work function in the presence of two adsorbates (for example oxygen and cesium), which as already stated are not discussed here.

In closing these brief remarks, it is fair to state that the progress which has been made with regard to the theoretical understanding of surface properties has provided us with sufficient insight to recognize many new, exciting and challenging problems.

APPENDIX

A CORRELATION FOR THE PREDICTION OF BARE WORK FUNCTIONS

The purpose of this appendix is to discuss briefly the correlation for bare work functions proposed in reference 17.

From the arguments presented in references 2, 17, and 25, it is concluded that, at T equals zero, the work function ϕ^* of a pure uniform surface equals the neutral orbital electronegativity $x_s(0)$ of a valence spin-orbital localized around a surface lattice-site and, therefore, ϕ^* would be known if $x_s(0)$ were known. The electronegativity at zero temperature may be computed by a direct extension to surface orbitals

of a correlation which has been derived for orbitals of atoms in a molecule.

To this end, it is noted that according to the works of Gordy²⁶ and of Pritchard and Skinner,²⁷ the neutral orbital electronegativity $x(0)$ of an atom in a molecule can be approximated by the relation

$$x(0) = 0.98 \frac{v+1}{r} + 1.57 \text{ (ev)}, \quad (\text{A-1})$$

where v is the number of electrons per atom which participate in bonding, and r is the effective size in Å of the atom in the bonded state.

Now, it is assumed that relation A-1 is also applicable to surface orbitals and, consequently,

$$\phi^* = x_s(0) = 0.98 \frac{v_s + 1}{r_m} + 1.57 \text{ (ev)}, \quad (\text{A-2})$$

where v_s is the number of electrons per surface atom which participate in bonding, and r_m is the effective size of these atoms in Å. The quantity v_s will be referred to as the surface valence.

The effective size of atoms on the surface is assumed to be equal to the atomic radius given by Slater.⁸ The surface valence, v_s , is derived from the metallic valence v_m and fractional bond numbers of atoms in the bulk, as discussed below.

Surface Valence. The metallic valence, v_m , is defined as the number of electrons per atom which participate in bonding in the bulk of a metal. The fractional bond number, n , is defined²⁸ such that $2n$ equals the average number of bonding electrons shared by two interacting atoms at an interatomic separation R . According to Pauling²⁹,

the fractional bond numbers n_1 and n_2 associated with the interatomic separations R_1 and R_2 , respectively, satisfy the following empirical relation:

$$R_2 - R_1 = 0.26 \ln(n_1/n_2). \quad (\text{A-3})$$

For body centered cubic (BCC), and for closed packed hexagonal (CPH) crystal structures, fractional bond numbers between atoms further distant than next-nearest neighbors are negligible. For face centered cubic (FCC) crystal structures, fractional bond numbers between atoms further distant than nearest neighbors are negligible. Thus, for each crystal structure, metallic valence and fractional bond numbers are interrelated as follows:

$$\text{BCC:} \quad v_m = 8n_a + 6n_b ; \quad (\text{A-4a})$$

$$\text{CPH:} \quad v_m = 6n_a + 6n_b ; \quad (\text{A-4b})$$

$$\text{FCC:} \quad v_m = 12n_a , \quad (\text{A-4c})$$

where n_a and n_b are the fractional bond numbers for nearest and next-nearest neighbors, respectively. Tabulated values of metallic valences and interatomic distances can be used in Eqs. A-3 and A-4 to compute the fractional bond numbers n_a and n_b for different materials.

If it is assumed that the fractional bond numbers of atoms on the surface are identical to those of atoms in the bulk, then the surface valence, v_s , is given by a summation of the form:

$$\text{BCC:} \quad v_s = N_a n_a + N_b n_b ; \quad (\text{A-5a})$$

$$\text{CPH:} \quad v_s = N_a n_a + N_b n_b ; \quad (\text{A-5b})$$

$$\text{FCC:} \quad v_s = N_a n_a , \quad (\text{A-5c})$$

where N_a and N_b are the number of nearest and next-nearest neighbors of surface atoms, respectively. The numbers N_a and N_b are fixed by

the crystallographic orientation of the surface. Table A-I lists values of N_a and N_b for various crystallographic planes of the BCC, CPH and FCC structures.

In summary, v_s can be computed from known properties of metal through the procedure described above. Computed values of v_s and tabulated values of r_m can then be used in Eq. A-2 to calculate bare work functions.

Results. Equation A-2 has been used to compute bare work functions for a large number of metal surfaces. The values of metallic valences, atomic radii, and interatomic distances, used in the calculations, are given in Table A-2.

The results for tungsten, molybdenum, tantalum and rhenium are presented in Tables A-3 through A-6, respectively. These tables also contain experimental values derived from thermionic emission data. It is seen that the predicted work functions are in very good agreement with the experimental values.

Bare work functions of individual planes have not yet been measured for most metals. Predicted values for a number of metals of interest are presented in Table A-7.

A significant implication of Eq. A-2 is that the bare work function of a metal surface is determined by three factors: (a) the number of ligands possessed by an atom on the surface; (b) the interatomic distances between that atom and its ligands; and (c) the metallic valence. As indicated by the results, a surface exhibits a high bare work function when the number of ligands and the metallic valence are large, and the interatomic distances are small.

Table A-2
Properties of Atoms in the Bulk^{8,29}

Element	Metallic Valence, v_m	Atomic Radius, r_m (Å)	Interatomic Distances to Neighbors (Å)	
			Nearest, R_a	Next Nearest, R_b
W	6	1.35	2.74	3.16
Mo	6	1.45	2.72	3.15
Ta	5	1.45	2.86	3.31
V	5	1.35	2.62	3.02
Li	1	1.45	3.04	3.50
Ir	6	FCC 1.35	2.71	3.83
Pt	6	1.35	2.78	3.93
Ni	6	1.35	2.49	3.52
Au	5.56	1.35	2.88	4.07
Cu	5.56	1.35	2.56	3.62
Th	4	1.80	3.60	5.10
Re	6	CPH 1.35	2.74	2.76
Os	6	1.30	2.68	2.74
Zr	4	1.55	3.18	3.23
Ti	4	1.40	2.90	2.95

Table A-1
Ligands of Surface Atoms

Plane	Number of Neighbors	
	Nearest, N_a	Next-Nearest, N_b
110	BCC 6	4
112	5	3
100	4	5
111	4	3
116	4	3
111	FCC 9	
100	8	
110	7	
0001	CPH(c/a < 1.633) 3	6
1010	4	4

Table A-3

Bare Work Functions of Tungsten

Plane	Work Function, ϕ (ev)			
	Theory	Experiment		
110	5.50	5.29 ³⁰	5.35 ³¹	5.40 ³²
112	4.94	4.65	4.80	4.80
100	4.66	4.52	4.60	4.55
111	4.47	4.38	4.40	4.42
116	4.47	4.29	4.32	

Table A-4

Bare Work Functions of Molybdenum

Plane	Work Function, ϕ (ev)			
	Theory	Experiment		
110	5.23	5.00 ³¹	5.10 ³³	4.90 ³⁴
112	4.71	4.55		
100	4.44	4.40	4.40	4.35
111	4.27	4.10	4.15	4.18
116	4.27	4.00		

Table A-5

Bare Work Functions of Tantalum

Plane	Work Function, ϕ (ev)	
	Theory	Experiment
110	4.75	4.80 ³¹
112	4.31	4.3-4.4
100	4.08	4.15
111	3.94	4.00
116	3.94	3.90

Table A-6
Bare Work Functions of Rhenium

Plane	Work Function, ϕ (ev)	
	Theory	Experiment
0001	5.53	5.59 ³⁵
10 $\bar{1}0$	5.20	5.15

Table A-7
Predicted Bare Work Functions
for Various Metal Surfaces

Plane	110	112	100	111	0001	10 $\bar{1}0$
BCC						
Element						
V	4.97	4.50	4.28	4.11		
Li	2.78	2.66	2.61	2.58		
FCC						
Ir	4.84		5.20	5.56		
Pt	4.84		5.20	5.56		
Ni	4.84		5.20	5.56		
Au	4.65		4.99	5.32		
Cu	4.65		4.99	5.32		
Th	3.38		3.57	3.75		
CPH						
Os					5.59	5.34
Zr					4.04	3.89
Ti					4.29	4.13

REFERENCES

1. HATSOPOULOS, G.N.; KEENAN, J.H.; "Principles of General Thermodynamics." John Wiley, New York, (1965), Chapter 48.
2. GYFTOPOULOS, E.P.; HATSOPOULOS, G.N.; "Quantum-Thermodynamic Definition of Electronegativity," Proc. National Academy of Sciences, July (1968).
3. HERRING, C.; NICHOLS, M.H.; "Thermionic Emission." Rev. Modern Physics 21(1949), p. 239.
4. BARDEEN, J.; "Theory of the Work Function, II. The Surface Double Layer," Phys. Rev. 49 (1936) p. 653.
5. LOUCKS, T.L.; CUTLER, P.H.; "The Effect of Correlation on the Surface Potential of a Free Electron Metal," J. Phys. Chem. Solids, Pergamon Press, 25 (1964), p. 105.
6. JURETSCHKE, H.J.; "Exchange Potential in the Surface Region of a Free-Electron Metal," Phys. Rev. 92, (1953) p. 1140.
7. GADZUK, J., "Many-Body Theory of a Rapidly Varying Inhomogeneous Electron Gas," NASA-PM-67 (1967).
8. SLATER, J.C., "Quantum Theory of Molecules and Solids," Vol. 2, McGraw-Hill, New York, (1965).
9. SMOLUCHOWSKI, R., "Anisotropy of the Electronic Work Function of Metals," Phys. Rev. 60 (1941) p. 661.
10. KOSKINEN, M.F.; "A Comparison of Two Theories of Cesium Adsorption," Proc. First International Conference on Thermionic Electrical Power Generation, London (1965) Paper 6-7.
11. BRIDGMAN, P.W.; "The Thermodynamics of Electrical Phenomena in Metals and a Condensed Collection of Thermodynamic Formulas," Dover Publications, New York (1961).
12. WIGNER, E.; BARDEEN, J.; "Theory of the Work Functions of Monovalent Metals," Phys. Rev. 48 (1935) p. 84.
13. GORDY, W.; THOMAS, W.J.O.; "Electronegativities of the Elements," J. Chem. Phys. 24 (1955) p. 439.
14. SACHTLER, W.M.H.; "Halbempirische Methode für Berechnung des Elektronen Austrittspotentials von Metallen," Z. Electrochem. 59 (1959) p. 119.

15. DEMCHENKO, V. V.; KHOMOTOV, N. E.; Tr. Mosk, Khim. - Technol. Inst. No. 39 (1962) p. 115.
16. RASOR, N.; WARNER, C., III; "Correlation of Electron, Ion and Atom Emission Energies," Atomics International Report AI-6799 (1961) p. 46.
17. STEINER, D.; GYFTOPOULOS, E. P.; "An Equation for the Prediction of Bare Work Functions," Report 27th Annual Conference Physical Electronics, MIT, Cambridge (1967) p. 160.
18. GADZUK, J. W., "Theory of Atom-Metal Interactions," Surface Science 6 (1967) p. 133.
19. RASOR, N.; WARNER, C., III; "Correlation of Emission Processes for Adsorbed Alkali Films on Metal Surfaces," J. Appl. Phys. 35 (1964) p. 2589.
20. GYFTOPOULOS, E. P.; STEINER, D.; "Orbital Electronegativity and Physical Properties of Bimetallic Adsorption Systems," Report 27th Annual Conference Physical Electronics, MIT, Cambridge (1967) p. 169.
21. GYFTOPOULOS, E. P.; LEVINE, J. D.; "Work Function Variation of Metals Coated by Metallic Films," J. Appl. Phys. 33 (1962) p. 67.
22. LEVINE, J. D.; GYFTOPOULOS, E. P.; "Adsorption Physics of Metals Partially Covered by Metallic Particles, II: Desorption Rates of Atoms and Ions," Surface Science 1 (1964) p. 225.
23. LEVINE, J. D.; GYFTOPOULOS, E. P.; "Adsorption Physics of Metals Partially Covered by Metallic Particles, Part III: Equations of State and Electron Emission S-Curves," Surface Science 1 (1964) p. 349.
24. LEVINE, J. D.; GYFTOPOULOS, E. P.; "Adsorption Physics of Metallic Surfaces Partially Covered by Metallic Particles, I: Atom and Ion Desorption Energies," Surface Science 1 (1964) p. 171).
25. GYFTOPOULOS, E. P.; HATSOPOULOS, G. N. "Quantum - Thermodynamic Meaning of Electronegativity and Work Function, Proc. Second International Conference on Thermionic Electrical Power Generation, Stresa, Italy (1968) Paper K-2.

26. GORDY, W. E. ; "A New Method of Determining Electronegativity from Other Atomic Properties," Phys. Rev. 69 (1946) p. 604.
27. PRITCHARD, H. O. ; SKINNER, H. A. ; "The Concept of Electronegativity," Chem. Rev. 55 (1955) p. 757.
28. COULSON, C. A. ; "Valence," Oxford University Press, London, 2nd Edition, (1961) p. 336.
29. PAULING, L. ; "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 3rd Edition (1960) p. 393-448.
30. SMITH, G. F. ; "Thermionic and Surface Properties of Tungsten Crystals," Phys. Rev. 94 (1954) p. 295.
31. PROTOPOPOV, O. D. et al. ; "Emission Parameters of Tantalum and Molybdenum Single Crystals," Soviet Phys. -Solid State 8 (1966) p. 909.
32. AZIZOV, U. V. ; SHUPPE, G. N. ; "Emission and Adsorption Characteristics of Faces of a Tungsten Single Crystal," Soviet Phys. -Solid State 7 (1966) p. 1591.
33. AZIZOV, U. V. ; et al. ; "Emission Properties of a Molybdenum Single Crystal," Soviet Phys. -Solid State 7 (1966) p. 2232.
34. SAVITSKII, E. M. ; et al. ; "Anisotropic Work Function of Molybdenum Single Crystals," Soviet Phys. -Technical Phys. 11 (1967) p. 974.
35. WICHNER, R. ; PIGFORD, T. H. ; "Work Function of Monocrystalline and Polycrystalline Rhenium," Report Thermionic Convention Specialist Conference, Houston (1966) p. 405.