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EFFECTS OF ARRIVAL RATES OF ABSORBATE IONS AND ATOMS ON SURFACE COVERAGE, HENCE WORK FUNCTIONS, OF EMITTING ELECTRODES

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SUMMARY

This report gives equations for determining substrate surface coverages from arrival rates and desorption characteristics of adsorbate ions and atoms. With a correlating theory by Gyftopoulos and Steiner, these coverages yield estimates of work functions for emitting electrodes with partial monolayers of other metals on their surface.

INTRODUCTION

Experimental and theoretic work relate changes in work functions φ of substrates s to fractional surface coverages θ of adsorbed films f (refs. 1 and 2). The latest and perhaps most effective method for predicting work functions of bimetallic systems comes from reference 3:

$$\varphi = \varphi_s - (\varphi_s - \varphi_f)M(\theta) + b(\theta)F(\theta) \tag{1}$$

Besides depending on coverage, M, b, and F involve physical properties of the substrate atoms and adatoms and their configurations (ref. 3). With the prescribed physics, the work function derives directly from the fraction of the substrate covered by adsorbed ions and atoms.

But predicting surface coverage from arrival rates at an emitting electrode contacting a plasma is a problem. In thermionics, for example, many investigators yet use the atom arrival rate alone, indicated by the cesium reservoir temperature, to estimate characteristics of emitters with positive-ion sheaths. Under these conditions cesium ions play an obviously important part in determining work functions.

More sophisticated attempts to approximate surface coverages led to subtler difficulties. Again in thermionics, a problem stems from the persistent improper use of the

Schottky equation. This expression equates the difference of ion and atom desorption energies to the work function of the substrate minus the ionization potential of the adsorbate. The Schottky equation describes a monometallic system (ref. 4), not a bimetallic one (refs. 4 to 8).

Thus, the application of equation (1) to an electrode in a plasma requires more than is presently at hand - at least, in thermionics. To assist in such studies, this report presents a general expression for fractional surface coverage as a function of arrival rates and desorption times and energies for the adsorbate ions and atoms. Equations for arrival rates caused by collisionless emission sheaths (refs. 9 to 11) indicate ionic effects and corrections.

SYMBOLS

b	function of θ
E_d	desorption energy
E_E	electric field at electrode
e	electronic charge
F	function of θ
I	ionization potential
j	current density
M	function of θ
N	number of free sites on clean surface
n	surface density of particles
P	desorption probability
T	absolute temperature
ΔV	electronic potential change across sheath
θ	fraction of substrate surface covered by adsorbate
κ	Boltzmann constant
μ	particle arrival density, arrival rate per unit area
ν	particle departure density, desorption rate per unit area
τ	desorption time
τ_o	coefficient in equation for desorption time

ω statistical weight of particle

Subscripts:

a atom

d desorption

E electrode

f adsorbate film

i ion

P plasma

THEORY

As reference 8 indicates, the Saha-Langmuir equation gives the ratio of rates of desorption for adsorbate ions ($j_{iE} = eP_i n_i$) and atoms ($j_{aE} = eP_a n_a$):

$$\frac{j_{iE}}{j_{aE}} = \frac{P_i n_i}{P_a n_a} = \left(\frac{\omega_i}{\omega_a}\right) \exp\left[\frac{e(\varphi - I)}{\kappa T_E}\right] \tag{2}$$

The desorption probability equals the reciprocal of the average desorption time τ, a function of the desorption energy E_d, and the coefficient τ_o:

$$P = \frac{1}{\tau} = \frac{1}{\tau_o} \exp\left(-\frac{E_d}{\kappa T_E}\right) \tag{3}$$

Of course, both E_d and τ for atoms and ions are function of surface coverage in bimetallic systems. Reference 1 tabulates some experimental τ_o's and "initial" values of E_d.

The sum of ionic and atomic surface densities of the adsorbate is the total coverage:

$$N\theta = n_i + n_a \tag{4}$$

Thus,

$$n_i = \frac{n\theta}{1 + \frac{n_a}{n_i}}$$

and (5)

$$n_a = \frac{N\theta}{1 + \frac{n_i}{n_a}}$$

Equations (2) and (3) yield the ratio of ionic to atomic coverages:

$$\frac{n_i}{n_a} = \left(\frac{P_a \omega_i}{P_i \omega_a}\right) \exp\left[\frac{e(\varphi - I)}{\kappa T_E}\right]$$

$$= \left(\frac{\tau_{oi} \omega_i}{\tau_{oa} \omega_a}\right) \exp\left[\frac{E_{di} - E_{da} + e(\varphi - I)}{\kappa T_E}\right] \quad (6)$$

The desorption rate ν, therefore, becomes

$$\nu = \frac{j_{iE} + j_{aE}}{e} = n_i P_i + n_a P_a = N\theta \left(\frac{P_i}{1 + \frac{n_a}{n_i}} + \frac{P_a}{1 + \frac{n_i}{n_a}} \right)$$

$$= N\theta \left\{ \frac{\frac{1}{\tau_{oi}} \exp\left(-\frac{E_{di}}{\kappa T_E}\right)}{1 + \frac{\tau_{oa} \omega_a}{\tau_{oi} \omega_i} \exp\left[-\frac{E_{di} - E_{da} + e(\varphi - I)}{\kappa T_E}\right]} + \frac{\frac{1}{\tau_{oa}} \exp\left(-\frac{E_{da}}{\kappa T_E}\right)}{1 + \frac{\tau_{oi} \omega_i}{\tau_{oa} \omega_a} \exp\left[\frac{E_{di} - E_{da} + e(\varphi - I)}{\kappa T_E}\right]} \right\} \quad (7)$$

Although reference 3 correlated E_{da} with θ for cesium and tungsten on a theoretic basis, at present, only experiments properly determine the E_d's and τ_o's (ref. 8). With these data and the desorption rate, fractional surface coverages result from equation (7), and then work functions come readily from reference 3. Unfortunately, no reasonably complete sets of experimental values for ionic and atomic E_d's and τ_o's exist. Langmuir's work is still the most comprehensive, but at best it lacks crystal specificity.

In a steady-state system, the total desorption rate of the adsorbate equals the sum μ of the arrival rates of adsorbate ions and atoms at the substrate surface. But, if an emitting electrode contacts a plasma, the arrival rate depends on the intervening sheath, which manifests the interaction of the electrode and the plasma (refs. 3 to 11). Thus, in devices like the thermionic diode, arrival rates are functions of electronic potential changes ΔV across electron and positive-ion sheaths.

For the electron sheath (ΔV is a negative number),

$$\nu = \mu = \frac{j_{aP} + j_{iP} \exp \frac{e\,\Delta V}{\kappa T_{iP}}}{e} \tag{9a}$$

For the positive-ion sheath (ΔV is a positive number, $\omega_i/\omega_a = 1/2$),

$$\begin{aligned}
\nu = \mu &= \frac{j_{aP} + j_{iP} + \left[1 - \exp\left(-\frac{e\,\Delta V}{\kappa T_E}\right)\right] j_{iE}}{e} \\
&= \frac{j_{aP} + j_{iP} + (j_{aP} + j_{iP})\left[1 - \exp\left(-\frac{e\,\Delta V}{\kappa T_E}\right)\right]}{e} \\
&= \frac{j_{aP} + j_{iP}}{e} \times \frac{1 + 2\exp\left[\frac{e(I - \varphi) + \left(e^3 E_E\right)^{1/2}}{\kappa T_E}\right]}{\exp\left(-\frac{e\,\Delta V}{\kappa T_E}\right) + 2\exp\left[\frac{e(I - \varphi) + \left(e^3 E_E\right)^{1/2}}{\kappa T_E}\right]}
\end{aligned} \tag{9b}$$

In equations (9), j_{aP} and j_{iP} are atomic and ionic current densities leaving the plasma and entering the sheaths. These are not necessarily random currents. The term containing j_{iE} in equation (9b) gives the ion emission reflected back to the emitter by the emission sheath; diagrams and explanations of the model appear in references 9 to 11. The electrostatic field at the electrode E_E enters equation (9b) through the Schottky effect, a lowering of the electronic emission barrier. These equations include the assumption of unit accommodation coefficients.

CONCLUDING REMARKS

Equation (9a) reveals that electric fields that retard emitted electrons reduce the effect of ions on the adsorbate arrival and desorption rates and, therefore, on the surface coverage and work function of the electrode. But equation (9b) shows that electric fields that accelerate emitted electrons increase the arrival rate of ions and thereby heighten the ionic influence on the work function. Thus, the tradition in thermionics of using the cesium reservoir temperature, hence, the atomic arrival rate alone, to predict work functions often yields poor approximations.

References 12 and 13 verify the importance of ion arrival rates in determining work functions. These experimental findings reveal ion currents of the order of atom fluxes entering sheaths from nonequilibrium cesium plasmas at conditions encountered in thermionic diodes. Ionic arrivals of this type appear as the j_{iP} terms in equation (9b). Even with no net currents, ion densities can increase by two orders of magnitude on moving from the plasma to the electrode through a 1-volt positive-ion sheath. References 9 to 11 show this effect for equilibrium and near-equilibrium sheaths. So the term containing j_{iE} in equation (9b) also exerts a strong influence on the work functions of electrodes contacting ionic-cesium sheaths. In general, good work-function estimates involve the sum of arrival rates for atoms, plasma ions, and reflected emitted ions if they occur.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 28, 1967,
123-33-02-01-22.

REFERENCES

1. Swanson, L. W.; Bell, A. E.; Hinrichs, C. H.; Crouser, L. C.; Evans, B. E.: Literature Review of Adsorption on Metal Surfaces. Vol. I and II. Field Emission Corp. (Contract NAS 3-8910), July 27, 1967.

2. Fomenko, V. S. (G. V. Samsonov, ed.): Handbook of Thermionic Properties. Plenum Press, 1966.

3. Gyftopoulos, E. P.; and Steiner, D.: Orbital Electronegativity and Physical Properties of Bimetallic Adsorption Systems. Report on 27th Annual Conference of Physical Electronics, Massachusetts Inst. Tech., Mar. 20-22, 1967, pp. 169-187.

4. Kaminsky, Manfred: Atomic and Ionic Impact Phenomenon Metal Surfaces. Academic Press, 1965.

5. Dobretsov, L. N.: Electron and Ion Emission. NASA TT F-73, 1963.

6. Varnerin, L. J., Jr.: Neutralization of Ions and Ionization of Atoms Near Metal Surfaces. Phys. Rev., vol. 91, no. 4, Aug. 15, 1953, pp. 859-863.

7. Hagstrum, Homer D.: Theory of Auger Ejection of Electrons from Metals by Ions. Phys. Rev., vol. 96, no. 2, Oct. 15, 1954, pp. 336-365.

8. Hughes, F. L.: Mean Adsorption Lifetime of Rb on Etched Tungsten Single Crystals: Neutrals. Phys. Rev., vol. 113, no. 4, Feb. 15, 1959, pp. 1036-1038.

9. Morris, James F.: Pairs of Emitter and Collector Sheaths for Cesium Thermionic Diodes. NASA TN D-4419, 1968.

10. Morris, James F.: Collisionless Sheaths Between Field-Modified Emitters and Thermally Ionized Plasmas Exemplified by Cesium. NASA TN D-4376, 1968.

11. Morris, James F.: Plane Collisionless Sheaths Between Field-Modified Emitting Electrodes and Thermally Ionized Plasmas Exemplified by Cesium. J. Appl. Phys., vol. 39, no. 2, Feb. 1968.

12. Breitwieser, R.: On the Relation of Ion and Electron Emission to Diode Diagnostics. Thermionic Conversion Specialists Conference, Gatlinburg, Tenn., Oct. 7-9, 1963, IEEE, pp. 17-26.

13. Houston, J. M.: Performance Characteristics and Emission Cooling Measurements Taken on a Cs Vapor Thermionic Converter with a Thorium-Tungsten Emitter. General Electric Co. (AFCRL-63-450), May 1963.

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