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DESORPTION KINETICS OF MULTIPLE ADSORBATES - CESIUM WITH FLUORINE ON MOLYBDENUM AND TUNGSTEN

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SUMMARY

Thermionic diodes containing multiple additives (both metallic and nonmetallic species) have received attention because of the increased durability of the surface layers and their low work functions. These factors promise low work function surfaces at higher temperatures or lower interelectrode gas pressures than can be achieved with metallic additives alone.

In the present report, the factors responsible for the enhanced durability of the multiple coating are examined. Activation energies for desorption of cesium from fluorinated molybdenum and fluorinated tungsten are deduced from experimental data. The fluorine serves to increase the activation energy for desorption of cesium from the surface. The energies for desorption of cesium from fluorinated molybdenum and fluorinated tungsten at low cesium coverages were found to be similar to the dissociation energy of the cesium fluoride molecule. For this reason, the desorption energies of cesium from halogenated surfaces should rank in the same order as the dissociation energy of the corresponding molecule.

Activation energies for the desorption of fluorine from tungsten and from molybdenum are also computed from published experimental data. A simple means of predicting these quantities for halogens on a variety of substrates is discussed, and values are presented. Hafnium and tantalum may bind the halogen layers more tightly than other refractory metals, with osmium binding more weakly. These contrasting properties may prove of value in construction of power-producing thermionic devices.

INTRODUCTION

Additives have for some time been known to influence favorably the performance of thermionic power-producing diodes. Some materials lower the space-charge barrier by existing as ions in the interelectrode space. In other cases, adsorption on surfaces causes a decrease in work function. Additives with either or both of these properties are generally electropositive materials such as alkali and alkaline earth metals.

Multiple additives (combinations of electropositive and electronegative atoms) can affect the emission of thermionic devices. Coatings of barium oxide and strontium oxide on tungsten (W) filaments were investigated by Moore and Allison (ref. 1), and by Gavriliuk (ref. 2). Coatings of cesium chloride on W filaments were investigated by Morgulis and Gavriliuk (ref. 3).

Recently, much interest has been shown in systems containing cesium and fluorine. Aamodt, et al. (ref. 4) and Ranken, et al. (ref. 5) studied the thermionic emission of a metal filament coated first with fluorine and then exposed to cesium vapor. Skeen (refs. 6 and 7) studied a thermionic diode simultaneously exposed to both cesium fluoride and cesium vapors. Reference 8 discusses a possible model for the structure of the surface layer in the adsorption of cesium on fluorinated molybdenum (Mo) in which cesium and fluorine are associated as erected cesium fluoride molecules on the surface.

These multiple adsorption systems in thermionic power-producing devices can confer several benefits. Work functions are lowered in some cases to values below those obtainable with the metallic adsorbate alone. Furthermore, the electronegative atoms appear in many cases to increase the bond strength of the electropositive atoms to the substrate, which results in a more durable coating. If the metallic additive (such as cesium) is supplied from a reservoir, a given work function can be maintained by a lowered interelectrode gas pressure with less electrical resistance. By the same token, surfaces of low work function can be obtained at elevated temperatures where excessive gas pressures would otherwise be required. If, on the other hand, the gaseous metallic additive is not continuously supplied, the lifetime of the low work function coating will be increased by reduced loss of the metal adsorbate atoms in the presence of the electronegative layer. For these reasons, the kinetics of desorption of the metallic and nonmetallic atoms from surfaces containing multiple additives are of interest.

Activation energies for desorption of cesium from fluorinated W and Mo deduced from published experimental data (refs. 4 and 5) are discussed herein. The results are compared with the heat of dissociation of the cesium fluoride molecule to develop a rough basis for making predictions for other alkali metal - halogen additive combinations.

In addition, activation energies for desorption of fluorine from Mo and W, determined from published experimental results, are presented. Analytical means of predicting these energies for halogen - metal combinations are discussed, and values are compared with experimental data where available.

By using these activation energies for desorption of cesium and halogens from metal surfaces in suitable rate equations, estimates of desorption rates can be made over a range of conditions. These rates may be useful in estimating the life of a halogen coating applied to a thermionic diode surface or in determining the rate at which the coating must be replenished for longterm operation.

DISCUSSION AND RESULTS

The benefits to be realized by halogenating thermionic converters containing cesium have aroused interest in the strength and nature of the cesium bond to the halogenated substrate. Little information exists as yet on the structure and the energetics of coatings consisting of more than one species. In reference 8, some evidence was presented for the erected dipole configuration for cesium (Cs) adsorbed on fluorinated Mo. An analysis of published experimental data indicates that Cs and fluorine (F) are associated as a molecule having the relation with the substrate shown in figure 1. The cesium fluoride

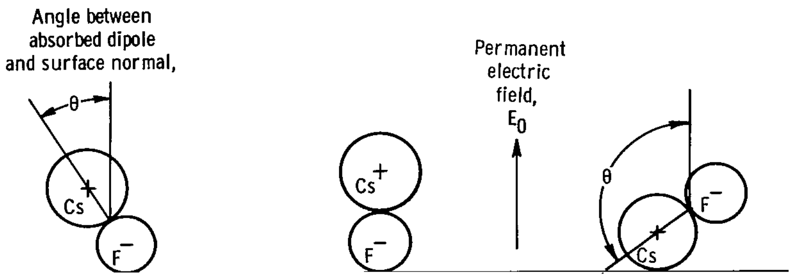

Figure 1. - Cesium fluoride molecule erected on surface with oscillation.

(CsF) molecule is assumed to be erected by a permanent electric field E_0. The molecules oscillate because of thermal agitation. The mean angular amplitude θ of the oscillation increases with temperature. It also increases with coverage because of the weakening of the permanent electric field by the fields of the dipoles.

In addition to structure, the activation energy for desorption of Cs from fluorinated metal substrates can be deduced from published data. Activation energies have been computed in the present study both for Cs on fluorinated Mo and for Cs on fluorinated W.

The durability of the F layer, which is related to its desorption kinetics, is also of obvious interest. Therefore, experimental activation energies for desorption of F from Mo and from W were obtained and compared with the energies calculated by simple theory. Although little reliable experimental data is available, the great promise of converters containing both Cs and F make careful analysis of these data desirable despite limitations.

Experimental Activation Energies for Desorption of Cesium from Fluorinated Molybdenum and Tungsten

Cesium on fluorinated molybdenum. - Aamodt, Brown, and Nichols (ref. 4) studied the thermionic emission of fluorinated Mo filaments exposed to Cs vapor. One of their figures is reproduced in figure 2, which contains curves of Cs arrival rate μ_a against reciprocal temperature $1/T$ for constant work functions.

An activation energy χ for the desorption of Cs from fluorinated Mo can be obtained from the figure. Figure 2 represents a steady-state condition for arrival and departure

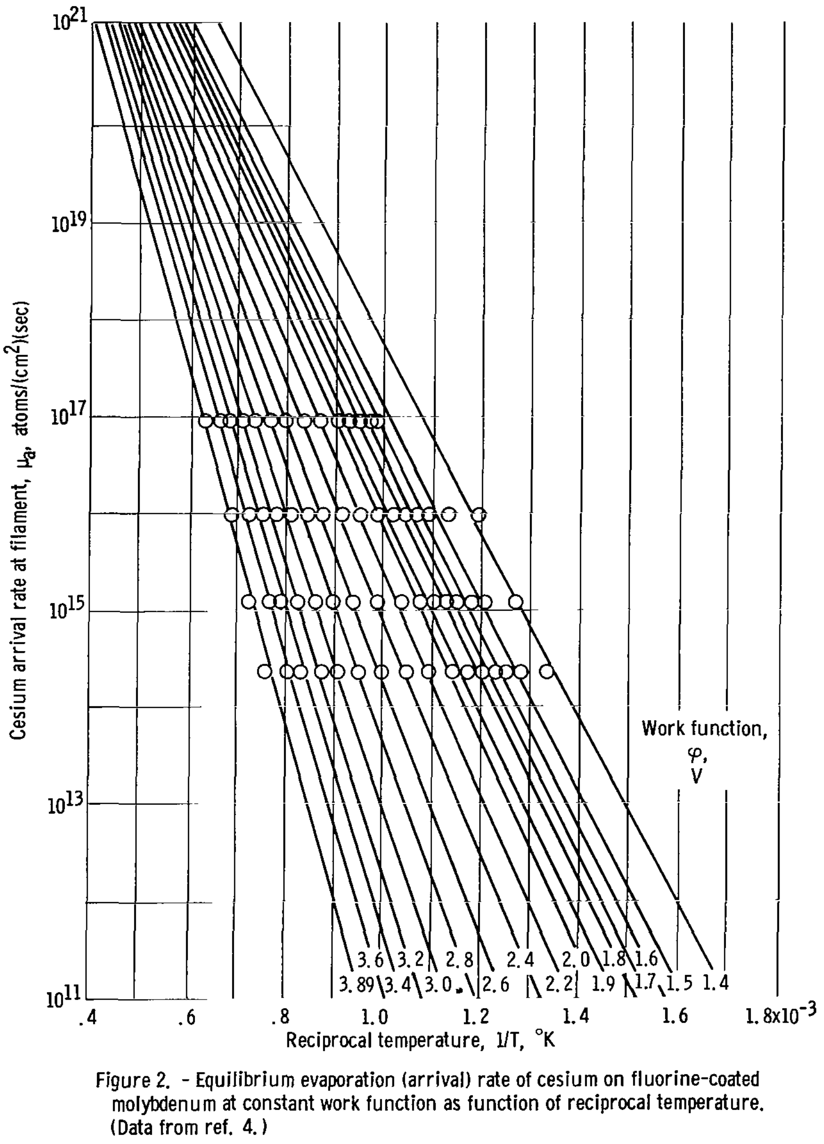

Figure 2. - Equilibrium evaporation (arrival) rate of cesium on fluorine-coated molybdenum at constant work function as function of reciprocal temperature. (Data from ref. 4.)

of Cs vapor, which can be described by the following simple relation (ref. 8, eq. (C18)):

$$\mu_a G(\sigma_1) = A\sigma_1 \exp\left(\frac{-\chi}{RT}\right) \tag{1}$$

where

A constant

$G(\sigma_1)$ condensation factor, $0 < G \leq 1$, herein taken as unity

σ_1 Cs concentration on fluorinated Mo, atoms/cm^2

R gas constant

(Symbols are also defined in appendix A.) In the erected dipole model, σ_1 represents the concentration of erected dipoles formed by the combination of adsorbed Cs and F.

Differentiation with respect to temperature at constant σ_1 gives

$$-R\left[\frac{\partial \ln \mu_a}{\partial(1/T)}\right]_{\sigma_1} = \chi \tag{2}$$

If φ is a function of Cs coverage and not of temperature, as is commonly assumed in the adsorption of Cs on bare metals, then

$$-R\left[\frac{\partial \ln \mu_a}{\partial(1/T)}\right]_{\varphi} = \chi \tag{3}$$

If χ is independent of temperature, ln μ_a is a linear function of 1/T (fig. 2). Values of χ obtained from figure 2 are plotted against φ in figure 3. (The data in fig. 3 were taken from ref. 4.) Shown for comparison is χ for Cs on unfluorinated Mo. This plot was taken from a graph of ln μ_a against 1/T, which is also contained in reference 4. The higher desorption energies for Cs on fluorinated Mo are evident. This enhancement of Cs desorption energy by the presence of adsorbed F is largely responsible for the increased durability of the multiple coating.

For Cs on fluorinated Mo, the assumption made previously that φ is a function of σ_1 alone may not be correct. In the erected dipole model for adsorption of Cs on fluorinated Mo (ref. 8), φ is a function of both σ_1 and T:

$$\varphi = \varphi(\sigma_1, T) \tag{4}$$

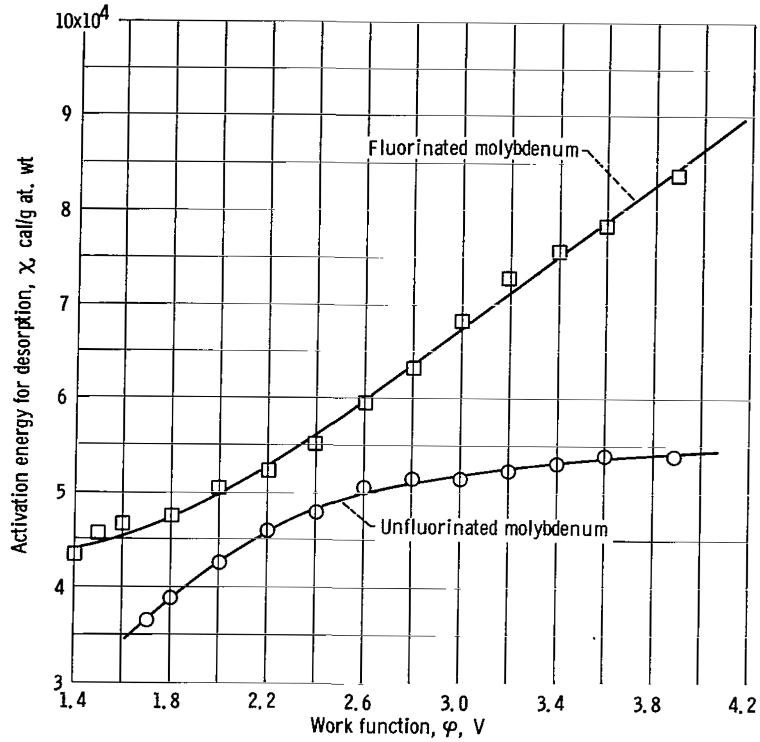

Figure 3. - Activation energy for desorption of cesium from fluorinated and unfluorinated molybdenum against work function. (Plotted from fig. 2.)

More explicitly, from equation (C1) of reference 8, the work function φ in volts is

$$\varphi = \varphi_0 - 4\pi\ 299.8\left[p_1\sigma_1 L(\eta) + \sigma_3 p_3\right] \tag{5}$$

where

p_1 magnitude of dipole moment of CsF (taken as constant) (stat C) (cm)

p_3 magnitude of dipole moment of F atom (taken as constant) (stat C) (cm)

φ_0 work function of bare surface, V

σ_3 concentration of F atoms, uncombined with Cs, that constitute nonoscillating dipoles

The Langevin function is defined as

$$L(\eta) = \coth \eta - \frac{1}{\eta} \tag{6}$$

where

$$\eta = \frac{p_1 E}{kT} \tag{7}$$

The erecting electric field is given by

$$E = E_0 - \beta\sigma_1^{3/2} p_1 L(\eta) - \beta\sigma^{3/2} p_3$$

where E_0 is the electric field of bare surface, statvolts per centimeter and β is the Topping constant (approx 9). The assumption was made in reference 8 that a monolayer concentration $\sigma_{3,m}$ of F was on the substrate. If every adsorbed Cs atom is associated with F to form a CsF molecule, the concentration of uncombined F atoms is

$$\sigma_3 = \sigma_{3,m} - \sigma_1 \tag{8}$$

Reference to equations (5), (6), (7), and (8) shows that the relation of equation (4) holds. In reference 8, $\sigma_{3,m}$ was taken to be about 1.0×10^{15} atoms per square centimeter.

If the erected dipole configuration is indeed applicable to the adsorption of Cs on fluorinated Mo, a relation exists between χ and $\partial \ln \mu_a/\partial(1/T)_\varphi$ other than that given by equation (3). As a consequence of equations (1) and (4),

$$\mu_a = \mu_a(\varphi, T) \tag{9}$$

Therefore,

$$\frac{-\chi}{R} = \left[\frac{\partial \ln \mu_a}{\partial(1/T)}\right]_{\sigma_1} = \left[\frac{\partial \ln \mu_a}{\partial(1/T)}\right]_{\varphi} + \left(\frac{\partial \ln \mu_a}{\partial \ln \varphi}\right)_T \left[\frac{\partial \ln \varphi}{\partial(1/T)}\right]_{\sigma_1} \tag{10}$$

From equation (5)

$$\left[\frac{\partial \ln \varphi}{\partial(1/T)}\right]_{\sigma_1} = -\frac{4\pi\ 299.8}{\varphi} p_1\sigma_1 L\left[\frac{\partial \ln L}{\partial(1/T)}\right]_{\sigma_1} \tag{11}$$

and from equations (C12) and (C14) of reference 8

$$\left[\frac{\partial \ln L}{\partial(1/T)}\right]_{\sigma_1} = \frac{T\left(\frac{d \ln L}{d \ln \eta}\right)}{\left(1 + \frac{\beta p_1 \sigma_1^{3/2}}{E} L \frac{d \ln L}{d \ln \eta}\right)} \tag{12}$$

where

$$\frac{d \ln L}{d \ln \eta} = -\frac{\eta}{L}\left(\operatorname{csch}^2\eta - \frac{1}{\eta^2}\right)$$

In the present case the derivatives of $\ln \mu_a$ were obtained from figure 2 (p. 4) by graphical means. The results of evaluating equation (10) for the data of figure 2 over a range of T and σ_1 are shown in figure 4. The line for $T = 0$ is equivalent to assuming that $L = 1$ in equation (5) or that all dipoles are normal to the surface. As temperature is increased, the computed χ decreases. The spread with temperature decreases as coverage decreases. At vanishingly low coverage with the work function of fluorine alone on molybdenum taken to be 4.98 volts (ref. 4), χ converges on a value of about 106 000 calories per gram atomic weight for all values of T.

The great variation of activation energy χ with temperature, amounting to about

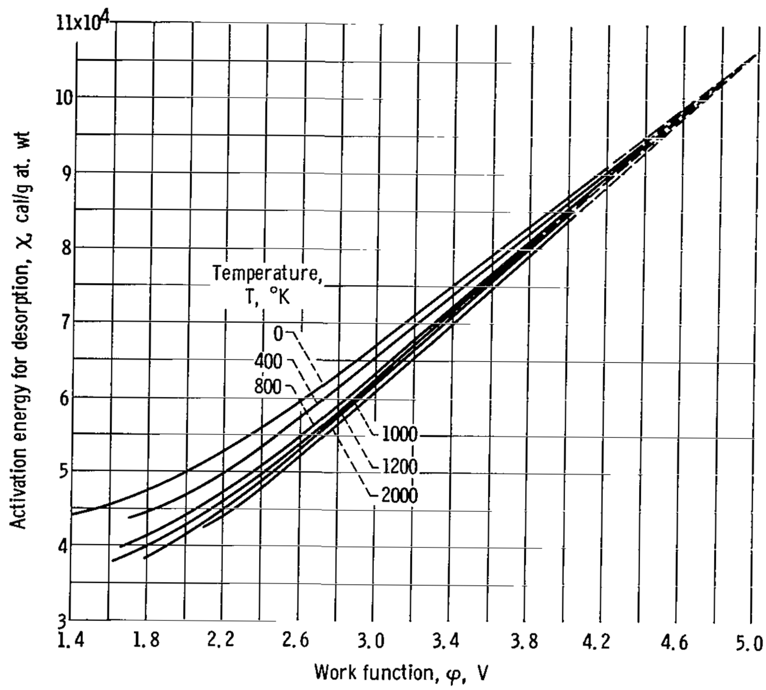

Figure 4. - Activation energy for desorption of cesium from fluorinated molybdenum against work function, corrected for erected dipole model at range of temperatures.

9000 calories at φ of 1.8 volt, is not to be expected. In part, it results from the necessity of using as the primary data source figure 2 (data from ref. 4). This figure was constructed from relatively meager thermionic emission data that were subject to much error as discussed in reference 4. In addition, the authors of reference 4 may have assumed in the preparation of their data that the lines of constant φ against ln μ_a and 1/T should be straight as is the case with monatomic adsorbates such as Cs. Consequently, the inclusion of a correction for the erected dipole in the computation of χ leads to the spread seen in figure 4. Less variation in χ would seem more probable with the temperature at fixed σ_1. Hence, the lines of constant φ in figure 2 should probably curve in such a manner that the spread in figure 4 is reduced.

Cesium on fluorinated tungsten. - The data of Rankin, Aamodt, Brown, and Nichols (ref. 5) enable an activation energy to be computed for the desorption of Cs from fluorinated W. A filament sealed within an evacuated tube was coated with CsF. The coating of CsF was progressively decomposed into Cs gas and adsorbed F by raising the filament temperature in increments. Temperature was maintained constant for some period of time at each level. The work function was measured photoelectrically just before the temperature was increased. The results of reference 5 are shown in table I, where $\Delta\varphi$ is measured relative to the bare metal work function (4.6 V). The data presented in the

TABLE I. - WORK FUNCTION DIFFERENCE OF CESIUM FLUORIDE COATED TUNGSTEN AGAINST FILAMENT TEMPERATURE

[Data from ref. 5.]

Filament temperature, ^{o}K	Work function difference, $\Delta\varphi$, V	Time at filament temperature, min	Adsorbate
659	-1.42	70	Fluorine and cesium
740	-1.50	↓	↓
814	-.28		
867	-.27		
903	-.18		
965	.09		
1025	1.42		
1085	1.60		
1150	1.67		
1225	1.77		
1309	1.86		
1420	1.86	70	Fluorine
1770	.53	11	Fluorine
1825	.24	11	Fluorine

table indicate that by the end of the run at 1309° K all the Cs had been driven off, and only an electronegative adsorbate was left on the surface. The electronegative material is assumed to be F, although there is some possibility of oxygen contamination, which will be discussed in the section entitled Fluorine on tungsten (p. 16).

For a simple analysis of the data in table I, the depolarization effect that is a consequence of the erected dipole model can be overlooked. This is equivalent to setting $L(\eta) = 1$ (eq. (5)). If the work function is assumed to be linear with the coverage of each species, the more correct equation (eq. (5)) relating work function φ to concentration σ_1 of erected CsF dipoles is replaced by

$$\Delta\varphi = \Delta\varphi_{1,m} \frac{\sigma_1}{\sigma_{1,m}} + \Delta\varphi_{3,m} \frac{\sigma_3}{\sigma_{3,m}} \tag{13}$$

where

$\Delta\varphi$ work function difference, $\varphi - \varphi_0$

$\Delta\varphi_{1,m}$ work function difference for monolayer of Cs on fluorinated W

$\Delta\varphi_{3,m}$ work function difference for monolayer of F on W

$\sigma_{1,m}$ concentration of Cs atoms in a monolayer on fluorinated W

The magnitudes of $\sigma_{1,m}$ and $\sigma_{3,m}$ are unimportant as they drop out in the final expression. Equation (8) is assumed applicable to the present case, thus equation (13) is made a function of $\Delta\varphi$ and σ_1 only.

A simple expression for the rate of single particle desorption given by Glasstone, Laidler, and Eyring (ref. 9, p. 354) can be written as

$$-\frac{d\sigma}{dt} = \sigma \frac{kT}{h} \frac{f_{\ddagger}}{f_a} \exp\left(\frac{-\chi}{RT}\right) \tag{14}$$

where

k Boltzmann's constant

h Planck's constant

$f_{\ddagger}$ partition function of activated complex

f_a partition function of adsorbed particle

The activated complex is described (ref. 9; p. 10) as a configuration intermediate between that of reactants and products, which are, in this case, the adsorbed particle and the free gas particle, respectively. Reference 9 indicates that if both the activated complex and adsorbed particles are immobile the ratio $f_{\ddagger}/f_a$ will be approximately unity. The quantity kT/h has a value of 2.08×10^{13} at 1000° K, which is of the same order as the vibrational frequency of strong chemical bonds in molecules and not much higher than the frequency of lattice vibrations in a solid (Hill, ref. 10, pp. 152-153 and p. 89). For the desorption of Cs from fluorinated W, the ratio $f_{\ddagger}/f_a$ will be assumed to be near unity. Equations (8), (13), and (14) are combined to give

$$-\frac{1}{\Delta\varphi - \Delta\varphi_{3,m}}\frac{d(\Delta\varphi)}{dt} = \frac{kT}{h}\exp\left(\frac{-\chi_1}{RT}\right) \tag{15}$$

Equation (15) is integrated with respect to time between t_A and t_B to obtain

$$\chi_1 = RT\left[\ln\frac{kT}{h}(t_B - t_A) - \ln\ln\frac{\varphi_{3,m} - \varphi_A}{\varphi_{3,m} - \varphi_B}\right] \tag{16}$$

The justification for replacing the Langevin function $L(\eta)$ by unity in equation (13) is now apparent in that $L(\eta)$ would appear in the log-log term to which χ of equation (16) is very insensitive.

The data of reference 5 in table I have been used to calculate an activation energy χ (from eq. (16)) for the desorption of Cs from fluorinated W presented in table II. (The CsF coverage parameter in table II is described in the next section.) In making the computation the amount of adsorbate lost between the cessation of a run at one temperature and the attainment of the next higher temperature must be assumed negligible. If this assumption is made, $\Delta\varphi$ measured at the termination of the lower temperature run applies at the beginning of the next run.

Comparison of activation energies for desorption of cesium from fluorinated molybdenum and fluorinated tungsten. - For the Cs-F-Mo system, illustrated in figure 4, no single curve can be considered as a representation of the correct χ for Cs on fluorinated Mo. For purposes of comparison, however, one curve must be singled out. In the absence of better insight, a curve at 1000° K will be chosen as correct. Furthermore, much cross plotting was done to the data in reference 4 and to the data herein prior to the construction of figure 4. All these manipulations of the data lead to possible error. In addition, the data in table I, the source of the data in table II for cesium on fluorinated tungsten, are subject to the possibility of oxygen contamination, which will be discussed in the section entitled Fluorine on tungsten (p. 16).

Since χ can be expected to vary with coverage, it follows that the data of figure 4

TABLE II. - ACTIVATION ENERGY FOR DESORPTION OF CESIUM FROM FLUORINATED TUNGSTEN

[Data from ref. 5.]

Filament temperature, ^{o}K	Activation energy for desorption, χ, cal/g at. wt	Cesium fluoride coverage parameter, $\varphi_{3,m} - \varphi$, V
814	64 100	2.76
867	76 200	2.16
903	75 500	2.08
965	78 500	1.90
1025	83 500	1.10
1085	85 700	.35
1150	92 100	.22
1225	96 200	.14
1309	102 200	.04

and of table II should be compared at roughly the same value of σ. Equations (5) and (8) can be solved for σ as a function of φ_1, which enables both sets of χ data to be plotted against σ_1. The many sources of error outlined previously would not seem to make it worthwhile. Instead, if $\Delta\varphi$ is assumed to vary linearly with σ_1, a parameter proportional to σ_1 is defined by combining equations (8) and (13) and solving for σ_1:

$$\sigma_1 = \frac{\Delta\varphi - \Delta\varphi_{3,m}}{\frac{\Delta\varphi_{1,m}}{\sigma_{1,m}} - \frac{\Delta\varphi_{3,m}}{\sigma_{3,m}}} = \frac{\varphi_{3,m} - \varphi}{\frac{\Delta\varphi_{3,m}}{\sigma_{3,m}} - \frac{\Delta\varphi_{1,m}}{\sigma_{1,m}}} \tag{17}$$

Assuming that the denominator is the same for both the Cs-F-Mo and Cs-F-W systems gives σ_1 proportional to $\varphi_{3,m} - \varphi$, defined now as the CsF coverage parameter. This parameter is included with the tabulation of χ for the desorption of Cs from fluorinated W in table II. The values of $\varphi_{3,m} - \varphi$ were computed by using the arithmetic mean of φ pertaining to the beginning and end of the run at each temperature. The value of $\Delta\varphi_{3,m}$ for F on W was assumed to be 1.86 volts, as suggested by table I. The work function of bare tungsten was taken as 4.6 volts.

In figure 5 a plot of χ against CsF coverage parameter $\varphi_{3,m} - \varphi$ is presented for the Cs-F-Mo system and for the Cs-F-W system. The Cs-F-Mo data at arbitrary temperatures of 1000° and 0° K are from figure 4. As suggested in reference 4, the value of $\Delta\varphi_{3,m}$ was equal to 0.6 volt for F on Mo, while the work function of bare Mo was 4.38 volts.

A downward trend with increased coverage parameter $\varphi_{3,m} - \varphi$ is seen in both the fluorinated Mo and fluorinated W data. At high values of $\varphi_{3,m} - \varphi$ the data for fluorinated Mo fall below those for fluorinated W. The difference is greatest for the 1000° K data, which incorporate the correction for the erected dipole assumption.

The variations of χ with work function given in figure 5 can be compared with the results of simple theory. Mignolet (ref. 11) presents an expression relating change in heat of adsorption with coverage to change in work function with coverage. Provided there is no activation energy for adsorption, Mignolet's expression can be used to obtain the following relation between χ and $\Delta\varphi$ in units of electron volts:

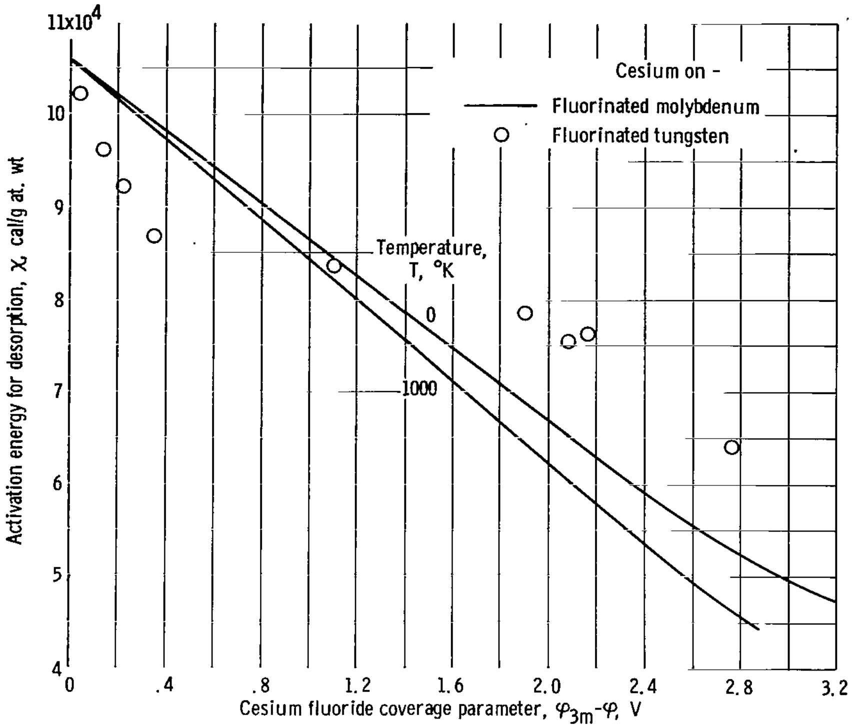

Figure 5. - Activation energy for desorption of cesium from fluorinated molybdenum and from fluorinated tungsten, against cesium fluoride coverage parameter.

$$\chi - \chi_0 = e\,\Delta\varphi \tag{18}$$

where χ_0 is the activation energy for desorption at vanishing coverage, and e is the magnitude of charge on the electron. Equation (18) will now be assumed to be applicable to multiple adsorbates. Bare surfaces with regard to Cs occur in figure 5 when $\varphi_{3,m} - \varphi$, the CsF coverage parameter, is zero. In equation (18), $\varphi - \varphi_{3,m}$ now replaces $\Delta\varphi$ for multiple adsorbates, or

$$\chi - \chi_0 = -e(\varphi_{3,m} - \varphi) \tag{19}$$

The Cs-F-Mo data of figure 5 are linear to a $\varphi_{3,m} - \varphi$ of about 2.4 volts. The corresponding $\chi - \chi_0$ of equation (19) should be -2.4 electron volts or -55 300 calories, which compares favorably with the difference of -52 500 calories, which can be computed from figure 5 for the same range of $\varphi_{3,m} - \varphi$ at 1000° K.

Comparison of activation energies for desorption of cesium from fluorinated metals with dissociation energy of gaseous cesium fluoride. - At the low Cs coverage limit defined by $\varphi_{3,m} - \varphi \rightarrow 0$, the data in figure 5 approach values of about 106 000 calories per gram atomic weight both for Cs on fluorinated Mo and for Cs on fluorinated W. A

TABLE III. - HEATS OF DISSOCIATION

OF CESIUM BLADES

[Data from ref. 12.]

Halide	Dissociation energy, cal/g at. wt
Cesium fluoride	116 000
Cesium cloride	101 800
Cesium bromide	91 000
Cesium iodide	76 300

comparison of this value with the heat of dissociation of the CsF molecule is interesting. The heats of dissociation reported for the cesium halides (ref. 12) are shown in table III. The dissociation energy of CsF and the activation energy for desorption of Cs from fluorinated Mo and W are about the same. The desorption of Cs from a halogenated substrate may involve essentially the breaking of the bond between the Cs and the halogen atom. If the erected dipole model is valid, this agreement would not be surprising.

Table III suggests that fluorine has a clear advantage over other halogens as a stabilizer of Cs coatings in thermionic devices.

Experimental Activation Energies for Desorption of Fluorine from Metals

Fluorine on molybdenum. - Reference 4 describes an experiment in which a Mo filament was coated with CsF as in the study with tungsten filaments in reference 5. The filament was flashed to 1200° F. This process decomposed the CsF and created a F layer on the filament. The presence of F, an electronegative element, was indicated by an increase of about 0.6 volt in thermionic work function. The filament was then raised to 1683° K, and the decay of work function with time due to fluorine desorption was measured. The temperature was raised in two further increments to 1785° and 1893° K without recoating, and the measurement repeated. The coating became more sparse as the temperature was progressively increased.

Adsorption lifetime τ can be computed from the fluorine desorption data of reference 4 by assuming that the work function difference of the F coating was linear with coverage so that

$$\Delta\varphi = \Delta\varphi_{3,m} \frac{\sigma_3}{\sigma_{3,m}} \tag{20}$$

This equation was substituted into an expression relating adsorption lifetime to the time rate of decay of coverage:

$$\frac{1}{\tau} = -\frac{d \ln \sigma_3}{dt} \tag{21}$$

Thus the following relation between τ and $\Delta\varphi$ is obtained:

$$\frac{1}{\tau} = - \frac{d \ln |\Delta\varphi|}{dt} \tag{22}$$

The lifetimes calculated in reference 4 for temperatures of 1683°, 1785°, and 1893° K are shown in table IV. The value of τ at 1785° K reported by these authors pertains to a collection potential of 9 volts. The additional value for τ at 1785° K was computed herein from data obtained before raising the collection potential to 9 volts. Table IV also contains activation energies for desorption of F from Mo computed from lifetimes by means of the following equation:

$$\frac{\chi}{RT} = \ln \frac{\tau kT}{h} \tag{23}$$

Equation (23) is obtained by combining equations (14) and (21) and by assuming that $f_{\ddagger}/f_a$ is unity.

The values of χ in table IV are in close agreement. This close agreement is not to be expected since surface coverage varied while the data of table IV were being taken. A work function difference variation between 0.6 and 0.066 volt was experienced in obtaining the data of table IV. For this variation, χ should change according to equation (18) by 0.53 electron volt or about 12 000 calories per gram atomic weight. The meager data available preclude conclusions that equation (18) does not apply to the adsorption of F on Mo or that equation (23) omits some variable sensitive to coverage.

TABLE IV. - ACTIVATION ENERGY FOR DESORPTION OF FLUORINE FROM MOLYBDENUM

[Computed from mean lifetime data of ref. 4 by means of eq. (23) of this report.]

Filament temperature, °K	Mean lifetime, τ, min	Activation energy (from eq. (23)), χ, cal/g at. wt
1683	[a]2536	144 200
1785	[a]308	145 700
1785	[b]392	146 500
1893	[b]31.7	146 200

[a]Collection potential, 3V.
[b]Collection potential raised to 9 V.

An alternate method for computing χ from lifetimes can be obtained by evaluating equation (23) for two temperatures. The difference of the resulting expressions may be taken, and the final result may be put in the form

$$\chi = \frac{RT_I T_{II}}{T_I - T_{II}} \ln \frac{\tau_{II} T_{II}}{\tau_I T_I} \tag{24}$$

where subscripts I and II denote data taken at two temperatures. This expression should be used only when the coverages σ were the same at the two temperatures for which the value of τ of equation (24) were obtained. By relaxing this restriction, however, the τ of table IV can be used to compute χ by using equation (24). Table V shows χ computed in this manner for various combinations of temperature T and lifetime τ.

TABLE V. - ACTIVATION ENERGY FOR DESORPTION OF FLUORINE FROM MOLYBDENUM

[Computed from mean lifetime data of ref. 4 by means of eq. (24) of this report.]

Filament temperature, T, °K		Mean lifetime, τ, min		Activation energy, χ, (eq. (24)) cal/g at. wt
Temperature, T_I	Temperature, T_{II}	Lifetime, τ_I	Lifetime, τ_{II}	
1785	1683	[a]308	2536	119 900
1785	1683	[b]392	2536	105 800
1893	1683	31.7	2536	128 600
1893	1785	31.7	[a]308	137 700
1893	1785	31.7	[b]392	152 700
				av: 128 900

[a]Collection potential, 3 V.
[b]Collection potential raised to 9 V.

The values of χ in table V are much more scattered than those in table IV. This scatter may be caused by the change in surface coverage and imposed experimental conditions during the time the data needed for the computation of table V were taken. The values do, however, fall within 30 percent of those in table IV.

Fluorine on tungsten. - From the data of reference 5, which are contained in table I (p. 9), a value of χ can be computed for the desorption of F from W. The data used are those taken at the three highest temperatures. The work functions taken at the end of the run at a given temperature are assumed to pertain also to the beginning of the run at the next higher temperature.

For the limited amount of data to be analyzed in this case, allowance can easily be made for a linear variation of χ with coverage in accordance with the equation

$$\chi = \chi_0 - \frac{\sigma_3}{\sigma_{3,m}} \Delta\chi_m \tag{25}$$

where $\Delta\chi_m$ is the coefficient for variation of χ with adsorbate coverage. The work function difference is also assumed to vary linearly with coverage in accord with equation (20). Equations (14), (20), and (25) are combined with the assumption that $f_{\ddagger}/f_a$ is unity to give the desorption rate equation:

$$-\frac{d \ln \Delta\varphi}{dt} = \frac{kT}{h} \exp\left[-\left(\frac{\chi - \frac{\Delta\varphi}{\Delta\varphi_{3,m}} \Delta\chi_m}{RT}\right)\right] \tag{26}$$

A similar expression for a desorption process was used by Moore and Allison (ref. 13).

Equation (26) can be integrated with respect to time, to obtain

$$E_1\left(\frac{\Delta\varphi_B}{\Delta\varphi_{3,m}} \frac{\Delta\chi_m}{RT}\right) - E_1\left(\frac{\Delta\varphi_A}{\Delta\varphi_{3,m}} \frac{\Delta\chi_m}{RT}\right) = \frac{kT}{h} (t_B - t_A)\exp\left(-\frac{\chi_0}{RT}\right) \tag{27}$$

The function

$$E_1(x) = \int_x^\infty \frac{e^{-t}\,dt}{t} = \int_x^\infty e^{-t}\,d \ln t$$

is tabulated in reference 14 (where t is a dummy variable not to be confused with time).

Using the data in table I for 1770° and 1825° K in equation (27) results in two equations that can be solved for the unknowns $\Delta\chi$ and χ_0. Such a computation gives

$$\Delta\chi_m = 20\ 700 \text{ cal}$$

$$\chi_0 = 141\ 700 \text{ cal}$$

This value of χ_0, nominally the low-coverage activation energy for desorption of F from W, compares favorably with the energies for desorption of F from Mo in table IV. The coefficient $\Delta\chi_m$ should correspond to a work function change of about 1 volt, according to equation (18). The $\Delta\varphi$ of 1.86 volts at 1420° K in table I corresponds to a $\Delta\chi$ of 1.86 electron volts or about 43 000 calories per gram atomic weight (eq. (18)).

The $\Delta\varphi$ of 1.86 volts associated with the electronegative adsorbate is one of two features of table I that should result in caution concerning the interpretation of data computed therefrom. The other is the long time, some 800 minutes, before the W filament was freed of Cs and desorption of the electronegative species began.

The $\Delta\varphi$ of 1.86 volts is far higher than the 0.6 to 0.8 volt reported for Mo coated by F (ref. 4) although the coating techniques were similar. A monolayer of F on W can be expected to have a work function difference similar to that of F on Mo. The maximum $\Delta\varphi$ measured for O adsorbed on W tips of a field emission microscope was 1.8 to 1.9 volts (ref. 15). This suggests the possibility of slow O contamination during the runs in table I. Consistent with this possibility are measured activation energies for desorption of O from W, variously reported as 147 000 ±3000 calories per gram atomic weight (ref. 16) and 141 000±22 000 calories per gram atomic weight (ref. 17), which compare favorably with the value of 141 000 calories per gram atomic weight deduced herein from the data in table I. Obviously, no assurance exists that a significant portion of the adsorbed species in table I is not oxygen.

Atomic or molecular nature of desorbing species. - The activation energies reported previously were assumed to be for the desorption of F atoms from Mo or W. Of course, the possibility exists that the desorbing species includes F molecules or fluorides of the substrate material. The nature of the species desorbing from W in the case of adsorbed halogens and O has been the source of speculation in the literature. Some of this discussion is summarized in appendix B. The conclusion is reached therein that F and O are most likely desorbed from Mo and W as atoms, at least for coverages of less than a monolayer.

Theoretical Activation Energies for Desorption of Halogens from Metal Substrates

Estimates of the desorption energy of halogens from metals may be desirable to elucidate the desorption mechanism in some experiment. These estimates may also be used to predict the suitability of possible substrate materials and additives in a gas-solid system for some particular application in the absence of experimental data.

In this section, theoretical activation energies for desorption of halogens from various metal substrates will be discussed. The results will be verified, where possible, by comparison with energies determined experimentally.

The following expression proposed by Eley (ref. 18), Haissinsky (ref. 19), and Stevenson (ref. 20) was used to compute the desorption energies for the halogens (fluorine (F), chlorine (Cl), bromine (Br), and iodine (I)):

$$D(M — X) = \frac{1}{2}\left[D(M — M) + D(X — X)\right] + 23\,000(x_M - x_X)^2 \qquad (28)$$

where

M	substrate species
X	nonmetallic adsorbed species
D(M—X)	dissociation energy of bond M—X and similarly for D(M—M) and D(X—X), cal/g mol. wt
x_M, x_X	electronegativities of elements

The term containing the electronegativities represents the contribution of the ionic part of the bond while the other term on the right represents covalency. The electronegativity is a semiempirical parameter tabulated for all the elements by Pauling (ref. 21), who first proposed the use of equation (28) to compute the strengths of molecular bonds.

For adsorption bonds, Eley (ref. 18) chose to relate the electronegativity difference $x_M - x_X$ to the work function change due to adsorption. Haissinsky (ref. 19) and Stevenson (ref. 20) criticize this practice and advocate, instead, using electronegativities from tabulations similar to those of Pauling. Eley (ref. 18), and Hayward and Trapnell (ref. 22) used equation (28) not only for cases of single adsorption bonds but for multiple bonds involving O and nitrogen (N), such as W═O and W≡N. Haissinsky, however, maintains that equation (28) can only be used for single adsorption bonds such as those involving halogens. For these reasons, equation (28) will be applied only to the computation of activation energies for the desorption of halogens from metals, with electronegativities taken from the tabulation of Pauling (ref. 21, table 3-8, p. 93).

The electronegativities of the halogens x_X and their dissociation energies D(X—X) required for the evaluation of equation (28) are listed in table VI.

The quantity D(M—M) must still be obtained for use in equation (28). This term represents the strength of the metal bonds broken in forming the surface. These atoms thereby become available for adsorption bonds. Appendix C shows that this strength is given approximately by the expression

$$D(M-M) = 0.127 \left(\Delta H_V + \frac{RT}{2}\right) \qquad (C7)$$

where ΔH_V is the heat of sublimation of metal in calories per gram atomic weight. This expression determines D(M—M) at that temperature T for which ΔH_V is specified.

TABLE VI. - DISSOCIATION ENERGIES AND

ELECTRONEGATIVITIES OF HALOGENS

Species	Dissociation energy,[a] D(X—X), cal/mole	Electronegativity,[b] x
Fluorine	37 800	4.0
Clorine	57 900	3.0
Bromine	46 100	2.8
Iodine	36 100	2.5

[a]Stull and Sinke (ref. 23) at 298° K.
[b]Pauling (ref. 21, table 3-8).

Table VII presents the values of the heat of sublimation ΔH_V and the electronegativity x for some metals of possible

TABLE VII. - HEATS OF SUBLIMATION, ELECTRONEGATIVITY, AND STRENGTH OF BROKEN SURFACE BONDS FOR SOME METALS

Metal	Crystal structure (a)	Heat of sublimation,[b] cal/g at. wt	Electro-negativity,[c] x	Strength of broken surface bond at 298° K, D(M—M), cal/g mol. wt
Hafnium	hcp	168 000	1.3	21 400
Tantalum	bcc	186 800	1.5	23 800
Tungsten	bcc	200 000	1.7	25 400
Rhenium	hcp	185 600	1.9	23 600
Osmium	hcp	160 000	2.2	20 400
Iridium	fcc	150 000	2.2	19 100
Platinum	fcc	134 800	2.2	17 200
Zirconium	hcp	146 000	1.4	18 600
Niobium	bcc	177 500	1.6	22 600
Molybdenum	bcc	157 500	1.8	20 000
Technetium	hcp	155 000	1.9	19 700
Ruthenium	hcp	144 000	2.2	18 300
Rhodium	fcc	133 000	2.2	16 900
Palladium	fcc	94 000	2.2	12 000
Cobalt	hcp	101 600	1.8	12 900
Nickel	fcc	101 300	1.8	12 900

[a]Hexagonal, closely packed, hcp; body centered cubic, bcc; face centered cubic, fcc.
[b]Stull and Sinke (ref. 23) at 298° K.
[c]Pauling (ref. 21, table 3-8).

interest. Strengths of the broken surface bonds D(M—M) computed from ΔH_v by equation (C7) are also shown for 298° K.

From the information in tables VI and VII, binding energies at 298° K were computed for some metal-halogen combinations by using equation (28). The results are listed in table VIII. Experimental activation energies for desorption χ are included for comparison where these are available. While the values of χ were determined at elevated temperatures, they can be compared with binding energies computed at 298° K because the temperature dependence of the latter is expected to be small.

Reference to table VIII indicates that reasonable agreement is found between D(M—X) and χ in the case of Cl on W and F on Mo. The agreement between D(M—X) and χ is somewhat poorer for F on W. As mentioned previously, reasons exist for questioning the purity of the desorbing species in the experiment of Ranken, et al. with F on W (ref. 5).

TABLE VIII. - BINDING ENERGIES OF HALOGEN ATOMS ON SOME SUBSTRATE METALS

Metal	Halogen adsorbate	Metal-adsorbate binding energy at 298° K, D(M—X), cal/g mol. wt	Experimental activation energy for desorption, χ, cal/g at. wt
Tungsten	Fluorine	153 300	[a]141 700
	Chlorine	80 500	74 000 to 82 000 (ref. 24)
	Bromine	63 600	----------------------
	Iodine	45 500	----------------------
Molybdenum	Fluorine	140 200	av 145 700 (table I)
	Chlorine	72 100	------------------
	Bromine	56 000	------------------
	Iodine	39 300	------------------
Hafnium	Fluorine	197 300	------------------
	Iodine	61 900	------------------
Tantalum	Fluorine	174 500	------------------
	Iodine	53 000	------------------
Osmium	Fluorine	103 600	------------------
	Iodine	30 300	------------------

[a]Calculated from data in ref. 5.

It must be recalled when comparing measured χ with measured D(M—X), that equation (28) for the latter is very sensitive to electronegativity x. The electronegativity, an empirically determined quantity, appears in a squared term. The electronegativity of a material will often vary depending on the source from which it was taken (e.g., refs. 21 and 25).

Referring to table VIII indicates that a vast spread in D(M—X) exists between values for F and I. Values for F were about twice those for Cl and about three times those for I. The values of D(M—X) for F and I on tantalum (Ta) and hafnium (Hf) are interesting in that they are about the highest values that can occur for these adsorbates according to equation (28). Responsible for the large binding energies, of course, is the very low electronegativity for these metals. The very high D(M—X) implies that the F-Hf coating may possibly persist to a higher temperature than that obtainable with any other substrate-adsorbate combination.

Relative to Hf and Ta, osmium (Os) has a very low binding energy for F and I. This may be a desirable property in some applications of halogens to a high-temperature device.

CONCLUDING REMARKS

The factors affecting the durability of multiple surface coatings in power-producing thermionic diodes were studied. Activation energies for desorption of Cs from fluorinated Mo and W were calculated from published data. At low coverages, these desorption energies approach the heat of dissociation of the CsF molecule, 116 000 calories per mole. This fact suggests that the desorption energies of Cs and other alkali metals from halogenated surfaces possibly rank in the same order as the dissociation energy of the corresponding alkali halide molecule.

Activation energies were also calculated from published experimental data for the desorption of F from Mo and W. Simple means of predicting desorption energies of atomic halogens from a variety of substrates were discussed. Estimated desorption energies of halogens from Hf and Ta were higher than those for the other refractory metals, while those for Os were lower than those of the other refractory metals.

Because of the growing interest in thermionic devices containing multiple additives such as F, experimental data are needed in addition to those available for the analysis herein. Not only are studies of coatings of alkali halides on metals meager, but few data exist for halogens adsorbed alone on metals.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 10, 1966,
123-33-62-02-22.

APPENDIX A

SYMBOLS

- a — lattice constant of crystal
- D — dissociation energy of diatomic molecule, as in D(X—X) pertaining to molecule X_2, cal/g mol. wt
- E — magnitude of surface electric field, stat V/cm
- E_0 — electric field of bare surface, stat V/cm
- $E_1(x)$ — function defined by $\int_x^\infty e^{-t}\, d \ln t$
- e — magnitude of charge on electron
- e^- — chemical symbol for an electron
- f_a — partition function of adsorbed particle (see ref. 9, p. 354)
- $f_\ddagger$ — partition function of activated complex (see ref. 9, p. 354)
- G — fraction of particles arriving at surface that are adsorbed
- ΔH_v — heat of sublimation, cal/g at. wt
- h — Planck's constant, 6.624×10^{-27} (erg)(sec)
- k — Boltzmann's constant, 1.3803×10^{-16} erg/$^{\circ}$K
- L — Langevin function (see eq. (6))
- M — electropositive or metallic species
- P — pressure
- p — magnitude of the moment of an electric dipole, (stat C)(cm) or debye
- R — gas constant, 1.9872 cal/(mole)($^{\circ}$K)
- S — surface area of a metal crystal specimen
- T — temperature, $^{\circ}$K
- t — time, sec
- W — work of creating new surface area
- X — electronegative or nonmetallic species
- x — electronegativity as given in ref. 21
- α — in metal, ratio of next-nearest neighbor bond strength ψ to nearest neighbor bond strength ξ
- β — Topping constant, approx 9
- γ — surface tension, erg/cm^2
- δ — surface volume per unit area, cm
- ϵ — surface energy, erg/cm^2
- η — independent variable in Langevin function defined by equation (7) for dipoles oriented by electric field
- θ — angle between adsorbed dipole and surface normal

μ_a	arrival rate of Cs atoms at surface regardless of whether adsorption occurs
ξ	strength of nearest neighbor bond in a metal, erg/bond
σ	surface density of adsorbed particles, particles/cm^2
τ	mean lifetime of particle on surface, sec
φ	work function, V
$\Delta\varphi$	work function difference, $\varphi - \varphi_0$, V
χ	activation energy for desorption, cal/g at. wt, or eV
χ_0	activation energy for desorption at vanishing coverage
$\Delta\chi_m$	coefficient for variation of χ with coverage
ψ	strength of next-nearest neighbor bond in a metal, erg/bond

Subscripts:

A	beginning of time interval
B	end of time interval
M	electropositive or metallic species
m	monolayer
X	electronegative or nonmetallic species
I, II	data taken at two temperatures
0	pertaining to bare surface
1	pertaining to adsorbed oscillating dipole of CsF
3	pertaining to nonoscillating adsorbed dipole of F

APPENDIX B

ATOMIC OR MOLECULAR NATURE OF DESORBING FLUORINE

The activation energies for desorption of fluorine from Mo and W reported previously are assumed to be for atoms. Of course, the possibility exists that molecular fluorine is involved. Another possibility is that molecules containing metal substrate atoms, such as MoF_6 or WF_6, are being desorbed.

Some disagreement exists in the literature as to the nature of the species desorbing from W in the case of halogens and oxygen. For instance, Silver and Witte (ref. 24) studied the desorption of chlorine from W tips in a field-emission microscope. They suggested that the desorbing material was a tungsten chloride.

Gomer and Hulm (ref. 15) observed the adsorption of oxygen on W tips in a field-emission microscope. They inferred that simultaneous desorption and oxidation occurred.

Schlier (ref. 26) studied the adsorption of oxygen on a W filament. He maintained that carbon contained in the filament resulted in the desorption of carbon monoxide rather than oxygen from the filament.

Johnson and Vick (ref. 16) advanced the concept of the adsorption and desorption of oxygen as atoms. Ehrlich (ref. 27) found their model and results acceptable.

Similarly, Eisinger (ref. 28) observed the adsorption of oxygen on W ribbons. He also concluded that oxygen was adsorbed as atoms. Moreover, for coverages of less than a monolayer, he believed that it desorbed as atomic oxygen, taking due cognizance of Schlier's view (ref. 26) concerning carbon monoxide desorption.

Evidence that halogens and oxygen desorb as atoms would seem to lie in measurement of the electron affinity of these gases. Electron affinity is defined as the energy of the reaction

$$X(gas) + e^-(gas) \rightarrow X^-(gas)$$

where X is an atom of halogen or oxygen, X^- is an ion, and e^- is an electron. In one type of measurement, the relative number of electrons, ions, and atoms leaving a hot filament of known temperature is found. Successful measurements with W filaments have been made of the electron affinity for all the halogen atoms (i.e., ref. 29, I; ref. 30, Cl; ref. 31, F, Cl, Br, and I) and for oxygen (ref. 32). The values for the halogens are in reasonable agreement with electron affinities obtained from observations of photodetachment thresholds for gaseous halogen atoms in a shock tube (ref. 33). Had any appreciable number of the atoms of the gas striking the hot filaments departed as W compounds, inconsistencies would probably have arisen in the electron affinity measurements.

Indeed, Bailey (ref. 31) raises just this argument concerning his own measurements for fluorine. He observed the species departing from the filament by means of a mass spectrometer. No WF^+ or WF^- ions were detected, nor was there any systematic trend in the electron affinity indicative of the desorption of tungsten fluorides.

Eisinger (ref. 28) makes a suggestion that may unify the discordant viewpoints of the adsorbate desorbing alone or in combination with substrate atoms. He maintained that a surface fully covered with oxygen would tend to have an increased probability of tungsten oxide formation and therefore W loss. The possibility exists that observations such as those of Silver and Witte (ref. 24) and Gomer and Hulm (ref. 15), indicative of tungsten loss with adsorbate desorption, might also involve high local concentrations of the adsorbate and consequent chemical attack. On the other hand, lower concentrations of adsorbate could result in negligible loss of substrate material.

Therefore, in experiments such as those of references 4 and 5 involving the desorption of fluorine at elevated temperatures from less than monolayer coverage, the desorbing species is probably atomic F. At conditions of greater than monolayer coverage, desorption of fluorine molecules and fluorides of substrate material may predominate.

APPENDIX C

STRENGTH OF SURFACE BONDS IN METALS

The strength of the bonds between like metal atoms in the metal interior can be computed from the heat of sublimation as discussed by Fricke (ref. 34) and Stranski and Suhrmann (ref. 35). In brief, the relations are as follows:

Face centered cubic (fcc) and hexagonal closely packed (hcp) metal crystals:

$$D(M-M) = \frac{\Delta H_v + \frac{RT}{2}}{6 + 3\alpha} \tag{C1}$$

Body centered cubic (bcc):

$$D(M-M) = \frac{\Delta H_v + \frac{RT}{2}}{4 + 3\alpha} \tag{C2}$$

where T is the temperature for which ΔH_v is specified, and α is the ratio of the strength of the next-nearest neighbor bond to the nearest neighbor bond in the crystal.

Values of α differ among various authors. Fricke (ref. 34) chose $\alpha = 0.01$ for fcc and 0.154 for bcc crystals. Stranski and Suhrmann (ref. 35) chose 0.5 for bcc. Ehrlich (ref. 27) accepted the value of 0.10 for hcp and fcc and 0.5 for bcc. The values of Ehrlich (ref. 27) were used in the calculations herein.

Bond strengths calculated by means of equations (C1) and (C2) apply to atoms in the metal interior. Evidence exists which indicates that the metal bonds broken to form the surface are weaker than the interior bonds. The strength of these broken metal bonds is to be employed in equation (28). From an examination of measured surface tension, Ehrlich (ref. 36) found that for fcc metals equation (C1) should be reduced by 20 percent. The corresponding factor for bcc metals will be computed in this appendix, based on experimental data for W and niobium.

A surface tension γ for crystalline W of 2900 ergs per square centimeter at 2000° K is reported in reference 37. Calverley (ref. 38) reports a γ of 2300 ergs per square centimeter for liquid W at 3380° C (melting point). For crystalline niobium, Radcliff (ref. 39) reports a value of γ of 2100 ergs per square centimeter at 2250° C. From these data, the surface energy ϵ can be computed.

Reference 40 (p. 12) gives the following equation for surface tension:

and for niobium

$$\xi = 1.62 \times 10^{-12} \text{ erg/bond}$$

Per gram atomic weight of bond, these values in calorie units are as follows:

Tungsten:

$$\xi = 25\ 630 \text{ cal/mole bond}$$

Niobium:

$$\xi = 23\ 330 \text{ cal/mole bond}$$

These latter numbers are to be interpreted as the experimental value of the strength of the broken surface bond D(M—M) required for the evaluation of equation (28).

On the other hand, the strength of the bonds in the interior of a bcc crystal are determined from equation (C2). For W at 2000° K, ΔH_v is 203 060 calories per mole, and for niobium ΔH_v is 175 750 calories per mole at 2523° K (Stull and Sinke, ref. 23). The strengths of interior bonds are as follows:

Tungsten:

$$D(M—M) = 37\ 280 \text{ cal/mole bond}$$

Niobium:

$$D(M—M) = 32\ 411 \text{ cal/mole bond}$$

The ratio of the strengths of surface to interior bonds are as follows:

Tungsten:

$$\frac{25\ 630}{37\ 280} = 0.688$$

Niobium:

$$\frac{23\ 330}{32\ 411} = 0.720$$

Thus, equation (C2) for bcc crystals must be multiplied by approximately 0.7 to give strengths for broken surface bonds in line with experimental information. This ratio will be assumed to be valid at all temperatures below the melting point. If equation (C2) is multiplied by this ratio for $\alpha = 0.5$ (ref. 27), the following expression is obtained for bcc metals:

$$D(M—M) = 0.127 \left(\Delta H_V + \frac{RT}{2}\right) \tag{C7}$$

On the other hand, if equation (C1) is multiplied by Ehrlich's value of 0.8 for the ratio of surface to interior bond strength for fcc metals (ref. 36) for $\alpha = 0.10$ (ref. 27), an equation identical to (C7) is obtained.

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