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LOW-COVERAGE HEATS OF ADSORPTION

III — ALKALI METAL IONS ON TUNGSTEN; ATOM-METAL INTERACTION THEORY

by Harold E. Neustadter and Keung P. Luke

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Cleveland, Ohio

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SUMMARY

The heat of adsorption of an ion on a metal (in the limit of zero coverage) is expressed as the superposition of a van der Waals type interaction and an image charge type interaction. The reported experimental values of the heat of adsorption of sodium, rubidium, and cesium ions on a tungsten substrate are then compared with results of a theoretical evaluation based on the above model.

INTRODUCTION

Considerable interest in alkali metal plasma for power generation and space propulsion has prompted extensive studies of adsorption of alkali metals on various substrates. A requirement for an adequate adsorption theory is the specification of the heat of adsorption in the limit of zero coverage. This report proposes an equation for calculating the heat of adsorption φ of an ion on a metal at coverages sufficiently low to allow neglect of interactions between neighboring adsorbed ions. Results of calculations based on this equation are compared with experimental values for sodium, rubidium, and cesium ions adsorbed on a tungsten substrate (table I). Note that attractive energies are denoted as positive.

TABLE I. - EXPERIMENTAL ZERO-COVERAGE HEATS OF ADSORPTION

Source	Sodium	Rubidium	Cesium
	Heat of adsorption, φ, ev		
Bosworth (ref. 1)	2.50		
Hughes and Levenstein (ref. 2)		1.90	
de Boer and Veenemans (ref. 3)			[a]2.36
Taylor and Langmuir (ref. 4)			[a]2.04
Becker (ref. 5)			2.19
Scheer and Fine (ref. 6)			2.04

[a] Not measured directly, but calculated from the assumption that all cesium adsorbed on tungsten exists only as ions.

SYMBOLS

a_0	Bohr radius
e	electron charge

k_m	defined by eq. (5)
n_o	free electron density of metal (tungsten)
R	distance from metal surface to center of ion
α	electronic polarizability
β	constant, ≈ 0.33
κ	defined by eq. (3)
φ	heat of adsorption of ion in limit of zero coverage
φ_i	defined by eq. (2)
φ_w	defined by eq. (4)

ANALYSIS

A model commonly used to explain the adsorptive bond approximates the adsorbed ion as a point charge and utilizes classical image-charge theory. This is an oversimplification in that (1) it neglects the contribution of the electronic distribution of the ion and (2) classical image-charge theory breaks down in the immediate region of the metal surface.

The adsorption energies can be treated as arising from the superposition of (1) the interaction φ_i of the net ionic charge with the metal and (2) a van der Waals type interaction φ_w of the instantaneous dipole moment of the ion with the metal. Thus,

$$\varphi = \varphi_i + \varphi_w \tag{1}$$

For φ_i a quantum mechanically corrected image-charge expression must be used, since the ions are 1/2 to 2 angstroms from the metal surface. Sachs and Dexter (ref. 7) have proposed such an expression:

$$\varphi_i = \frac{e^2}{4R} - \beta\kappa^{1/2}\frac{e^2}{4R^2} \tag{2}$$

where R is the distance from the surface to the center of the ion, β is a constant, and

$$\kappa = -\frac{1}{3}\left(\frac{3}{8\pi}\right)^{1/3} n_o^{-2/3} + \frac{(2\pi)^2}{6}\left(\frac{3}{8\pi}\right)^{2/3} a_o n_o^{-1/3} \tag{3}$$

in which n_o is the free electron density of the metal, and a_o is the Bohr radius.

The energy arising from the polarization of an adsorbed particle has been studied by Prosen and Sachs (ref. 8) and is given by[1]

$$\varphi_w = \frac{\alpha e^2 \pi k_m}{(2\pi)^3} \frac{\ln(2k_m R)}{R^2} \tag{4}$$

where α is the electronic dipole polarizability of the adsorbed ion (table II), and

$$k_m = (3\pi^2 n_o)^{1/3} \tag{5}$$

The complete expression for the heat of adsorption of ions on a metal in the limit of zero coverage is obtained by adding equations (2) and (4):

$$\varphi = \frac{e^2}{4R} - \beta\kappa^{1/2} \frac{e^2}{4R^2} + \frac{\alpha e^2 \pi k_m^2}{(2\pi)^3} \frac{\ln(2k_m R)}{R^2} \tag{6}$$

TABLE II. - ELECTRONIC POLARIZABILITY

Source	Sodium ion	Rubidium ion	Cesium ion
	Electronic polarizability, α, A^3		
Sternheimer (ref. 10)	[a]0.152	[a]2.920	[a]5.60
Fajan and Joos (ref. 11)	.196	1.56	2.56
Born and Heisenberg (ref. 12)	.210	1.81	2.79
Pauling (ref. 13)	.189	1.41	2.44
Tessman, Kahn, and Shockley (ref. 14)	.255	1.797	3.137

[a]Calculated.

Implicit in equation (6) and the choice of ionic values of polarizability is the assumption that a particle that desorbs as an ion has the properties of an ion prior to desorption. Hughes (ref. 15) in his adsorption-lifetime studies has found evidence to support this.

To apply equation (6), it is necessary to evaluate the constant β and R, the distance from the nucleus of the ion to the metal surface. The location of this "surface" is not well defined, however. Physically it is that plane on which all excess electrons would collect. The constant β depends on the choice of wave function used in deriving equation (2). Sachs and Dexter estimated β to be 0.46; however, their approximations appear to make this an upper limit. That this value of β is too high has been substantiated by others in two instances (ref. 16). Since β is not uniquely determined, this report evaluates it by matching the calculated value of φ for sodium adsorption to the reported experimental value. In the course of evaluating β, R will also be determined. The value of φ for sodium was selected because the electronic polarizability of the sodium ion is very small (table II). Thus,

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[1] The choice of equation (4) to express the van der Waals type interaction is based on the results of an earlier study by the authors of this report (ref. 9).

the contribution of φ_w to the heat of adsorption of sodium ions on tungsten is small ($\varphi_w \cong 0.04$ ev) and one can approximate

$$\varphi(Na^+ - W) = \varphi_i = 2.46 \text{ ev} \tag{7}$$

At equilibrium the sodium ion will be at that R value for which φ_i is a maximum. Taking

$$d\varphi_i/dR = 0 \tag{8}$$

gives the result

$$R = 2\beta\kappa^{1/2} \tag{9}$$

For tungsten (lattice constant of 3.16 A, one conduction electron per atom) $\kappa^{1/2} = 1.1$, and from equation (9) $R = 2.2\ \beta$. The constant β can now be evaluated by using this result in equations (7) and (2), the final results[2] being $\beta \cong 0.33$ and $R = 0.73$ A.

The use of a hard sphere model, the assumption of adsorption taking place on the (110) plane of tungsten, and the value $R = 0.73$ A, locate the metal surface at 0.93 A from the plane through the centers of the outermost layer of atoms (see fig. 1). This is 71 percent of the distance from the center of the surface layer of atoms to the outermost tangent of the surface layer of atoms, which is a physically reasonable result.

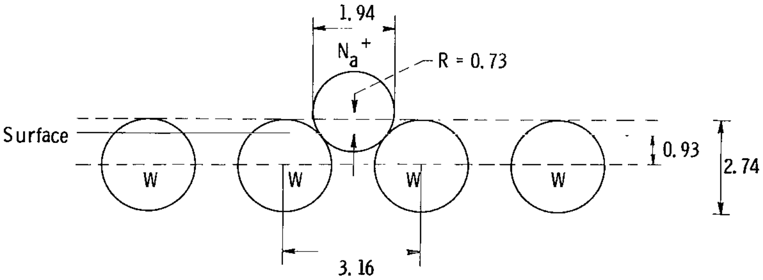

Figure 1. - Sodium ion adsorbed on a (110) plane of tungsten. (Dimensions in angstroms.)

Sufficient evidence justifies the assumption that for tungsten emitters the emitting surfaces were essentially (110) planes (refs. 4, 5, and 17). The distance R was also calculated for rubidium and cesium ions on tungsten by using the same hard sphere model, and assuming the value of β, and the location of the surface to be independent of the nature of the adsorbed ion.

Because α is not uniquely determined (table II), the calculation of φ was performed for both the most recently reported calculated values, and the average of all reported experimental values of α. The results are listed in

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[2] This value of β is slightly lower than the upper limit $\beta = 0.46$ suggested by Sachs and Dexter (ref. 7) and considerably higher than the value $\beta = 0.09$ used by Cutler and Gibbons (ref. 16), which is reasonable.

table III. In general, the calculated values of φ are in reasonable agreement with the experimental values. That the calculations based on the calculated values of α show a slightly lower value for the cesium ion - tungsten adsorption than for the rubidium ion - tungsten adsorption is particularly interesting. This is in agreement with the experimental results. While the major bonding is due to the image-force of the net charge of the ion, the polarization effect cannot be neglected. It is primarily the difference in polarizabilities that accounts for the heat of adsorption of cesium on tungsten being lower than that of rubidium on tungsten when the calculated values of α are used.

TABLE III. - APPLICATION OF EQUATION (6) TO ADSORPTION

OF ALKALI METAL IONS ON TUNGSTEN

Ion	Electronic polarizability, α, A^3	Distance from metal surface to center of ion, R, A	Interaction energy, φ_i, ev	Heat of adsorption, φ, ev	
				Calculated	Experimental
Sodium	[a]0.200	[a]0.73	[a]2.460	2.51	2.50
	[b]0.152			2.50	
Rubidium	[a]1.899	[a]1.44	[a]1.875	2.13	1.90
	[b]2.920			2.27	
Cesium	[a]3.305	[a]1.69	[a]1.660	2.03	2.04 to 2.19
	[b]5.600			2.29	

[a] Average of value listed in table II.

[b] Calculated.

CONCLUDING REMARKS

While equation (6) is not exact (the polarization term considers only dipole-dipole interactions), the results obtained (table III) are generally good. On the basis of the calculations performed, the theory presented is adequate to explain the phenomena of adsorption of alkali metal ions on tungsten in the limit of zero coverage and emphasizes that the effect arising from the polarizability of the adsorbed ion should not be neglected.

Unfortunately, the experimental values of φ had to be collected from a variety of experimental techniques and laboratory conditions of numerous workers. It must also be recognized that except for the cesium adsorption there is only one reported value of φ for each system. The results of this study must necessarily be considered within the framework of these limitations.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, May 27, 1964

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