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LOW-COVERAGE HEAT OF ADSORPTION

I — ALKALI METAL ATOMS ON TUNGSTEN; ATOM-METAL INTERACTION THEORIES

by Harold E. Neustadter and Keung P. Luke

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SUMMARY

A comparison of the experimental values of heat of adsorption (in the limit of zero coverage) for sodium, rubidium, and cesium on a tungsten substrate is made with those calculated from four different atom-metal theories. The best results are obtained from the theory developed by Prosen and Sachs, which takes into account the Fermi degeneracy of the electrons in the metal.

INTRODUCTION

The considerable interest in alkali metal plasma research for power generation and space propulsion has in turn prompted extensive studies of the adsorption of alkali metals on various substrates. A requirement for an adequate adsorption theory is the specification of the heat of adsorption at the limit of zero coverage. This report compares the experimental values of heat of adsorption φ for sodium, rubidium, and cesium on a tungsten substrate in the limit of zero coverage with four atom-metal interaction theories. A repulsive interaction factor is added to the four standard interaction theories, and comparisons are indicated.

Each of the theories includes two physical constants, the electronic polarizability of the adsorbed atom α and the distance R from the metal surface to the nucleus of the adsorbed particle. The value of the theories is established by determining if acceptable values of α and R result for the experimental values of φ. Acceptable values of α are from experimental results. For molecules that are an angstrom or two from the outermost layer of substrate atoms, the classical macroscopic approach breaks down, and the surface is no longer well defined. Therefore a hard-sphere model is adopted herein that takes into account the atomic nature of the exposed substrate surface. The process of preparing and aging, tungsten emitters transforms the exposed surface into essentially a (110) plane (refs. 1 to 3). Therefore, it is assumed herein that all the emitting surfaces were (110) planes (as in fig. 1). One would expect the surface to be located between the plane through

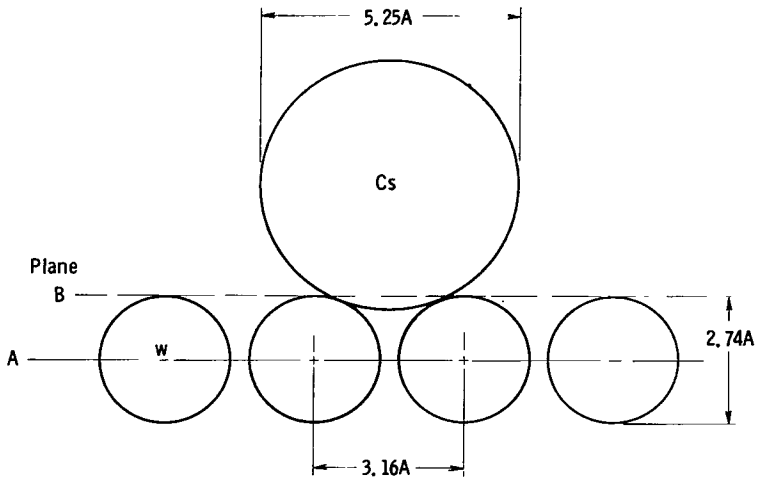

Figure 1. - Cesium atom adsorbed on (110) plane of tungsten surface.

the centers of the outermost layer of atoms in the tungsten metal (plane A of fig. 1) and the outer tangent to this layer of atoms (plane B of fig. 1).

ATOM-METAL INTERACTIONS

Four quantum-mechanical treatments of interaction of a nonpolar molecule with a metal surface are considered in this section. From each of these an interaction energy of adsorption φ will be calculated. Common to all are the following two assumptions:

(1) The correction to the unperturbed Hamiltonian is, in first approximation, due to the interaction of the field of the instantaneous dipole moment of the atom with the electrons and positive ions in the metal.

(2) The additional energy caused by the presence of the metal is of the nature of a perturbation.

The first to introduce this approach (1932) was Lennard-Jones (ref. 4). The perturbation was based on a multipole expansion for the neutral charge distribution of neutral atoms, where the dipole or first nonvanishing term was retained. The metal was replaced by its classical image-charge equivalent, and the dipole-dipole interaction of the incoming atom with its image was calculated. This formulation leads to the first-order energy correction

$$\varphi = \frac{mc^2\chi}{2R^3} \tag{1}$$

Symbols are defined in appendix A.

Bardeen (ref. 5) took into account the interaction of the electrons in the metal by averaging the energy of the molecule over the metal wave function. This was shown to be a second-order effect and results in

$$\varphi = \frac{\alpha I C e^2}{16\,R^3} \frac{1}{r_s I + \frac{Ce^2}{2}} \tag{2}$$

Margenau and Pollard (ref. 6) derived a second-order correction without

consideration of an image force. The metal was broken up into elementary portions. The energy was calculated for the interaction of the molecule with each elementary portion and then summed over the entire metal to give

$$\varphi = \frac{\alpha e^2}{16\ R^3}\left(\frac{2\hbar n_o}{m\nu} - \frac{C}{r_s}\right) \tag{3}$$

Most recently (1942) Prosen and Sachs (ref. 7) considered the second-order change in energy. In addition, they took into account the Fermi degeneracy of the electrons in the metal and arrived at the result

$$\varphi = \frac{\alpha e^2 k_m^2}{8\pi^2}\,\frac{\ln(2k_mR)}{R^2} \tag{4}$$

APPLICATION OF ATOM-METAL THEORIES

Equations (1) to (4) were derived with consideration of attractive forces alone. The repulsive forces arising from the overlapping of the electron clouds have been neglected. The approximate effect of these repulsive forces on the system energy decreases the values given in equations (1) to (3) by one-third and that given in equation (4) by two-ninths, where a repulsive force varying as R^{-9} is assumed. The derivation of this approximation is given in appendix B. Equations (1) to (4) are rearranged below to include this correction as well as the substitution of numerical values for m, c, C, n_o, k_m, and r_s.

$$\alpha = \frac{3}{2}\,5.88\times10^{-11}\,\frac{\varphi^2R^6}{n} \tag{1a}$$

$$\alpha = \frac{3}{2}\,0.692\left(1 + \frac{40.5}{I}\right)\varphi R^3 \tag{2a}$$

$$\alpha = \frac{3}{2}\,\frac{\varphi R^3}{0.9}\left(5.63 - \frac{6.05}{I}\right) \tag{3a}$$

$$\alpha = \frac{9}{7}\,3.63\,\frac{\varphi R^2}{\ln(2.46\ R)} \tag{4a}$$

The values of n_o, k_m, and r_s were calculated by assuming one conduction electron per tungsten atom. The value of χ was determined by the Kirkwood formula (ref. 8) as $\chi = mc^2\,(n\alpha)^{1/2}$.

Because the derivations of equations (1) to (4) neglected all attractive terms of higher order than the dipole-dipole term, introducing the correction for repulsive forces does not clearly constitute an improvement. As the distance between bodies decreases, the higher order terms in the multipole expansion become increasingly important. These neglected terms might be quite

TABLE I. - LIMITS IMPOSED ON DISTANCE FROM (110) TUNGSTEN SURFACE TO NUCLEUS OF ADSORBED ATOM

[Based on models shown in fig. 1.]

	Sodium		Rubidium		Cesium	
	Atom	Ion	Atom	Ion	Atom	Ion
Hard-sphere radius (ref. 9), A	1.857	0.95	2.44	1.48	2.625	1.69
Minimum distance R, A	1.5	.3	2.1	1.0	2.2	1.2
Maximum value of R, A	2.9	1.7	3.4	2.4	3.7	2.6

sizable for R in the neighborhood of 1 to 3 angstroms. This would provide a compensating error. Therefore, equations (1) to (4) were also calculated without corrections:

$$\alpha = 5.88\times10^{-11}\,\frac{\varphi^2 R^6}{n} \tag{1b}$$

$$\alpha = 0.692\left(1 + \frac{40.5}{I}\right)\varphi R^3 \tag{2b}$$

$$\alpha = \frac{\varphi R^3}{0.9}\left(5.63 - \frac{6.05}{I}\right) \tag{3b}$$

$$\alpha = 3.63\,\frac{\varphi R^2}{\ln(2.46\ R)} \tag{4b}$$

An equation of this group is applicable if a reasonable value of R (table I) and an experimental value of φ (table II) correspond to a value of φ that is within the range reported in the literature (table III).

TABLE II. - EXPERIMENTAL ZERO-COVERAGE HEATS OF ADSORPTION

Source	Sodium	Rubidium	Cesium
	Heat of adsorption, φ, ev		
Bosworth (ref. 10)	1.38[a]	---	----
Hughes (ref. 11)	----	2.6	----
deBoer and Veenemans (ref. 12)	----	---	3.0
Taylor and Langmuir (ref. 1)	----	---	2.79
Becker (ref. 2)	----	---	2.40

[a]Values of φ denoted as positive in this report.

TABLE III. - ELECTRONIC POLARIZABILITY

Source	Sodium	Rubidium	Cesium
	Electronic polarizability, α, A^3		
Salop, Pollack, and Bedesson (ref. 13)	20±2.5	40±5	52.5±6.5
Chamberlain and Zorn (refs. 14 and 15)	21.5±2	38±4	48±6
Sternheimer (ref. 16)	22.9	49.1	67.7

Examples of applicable and nonapplicable equations are shown in figures 2 and 3, respectively.

The calculations performed show that

(1) Equation (4) is applicable to all three adsorption systems considered. Its maximum error for α is under 40 percent in any of the systems, for any reported value of φ and in either "corrected" or "uncorrected" form. Equations (1) to (3) are not applicable because they introduce an error of greater than 100 percent.

(2) Best results are obtained from equation (4b). For cesium and rubidium adsorption, the values of α are within the range reported. For sodium the calculated value is 25 percent too low.

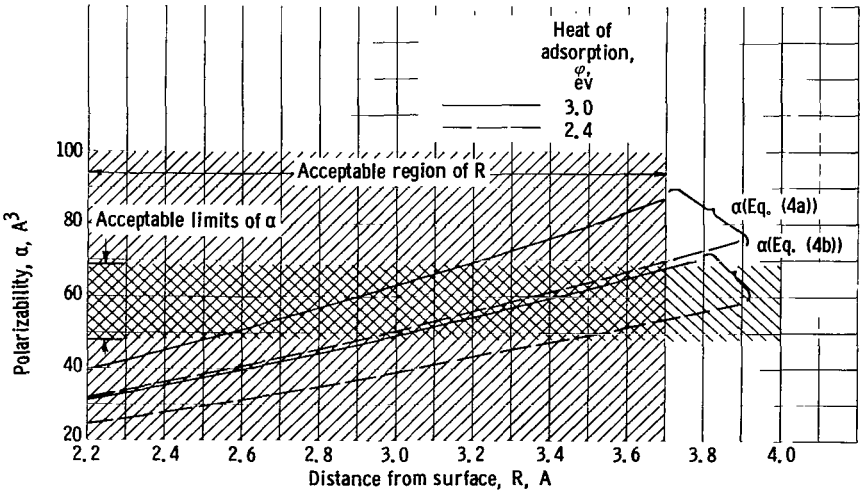

Figure 2. - Polarizability of adsorbed cesium atom plotted against distance from tungsten substrate, based on two applicable equations, (4a) and (4b).

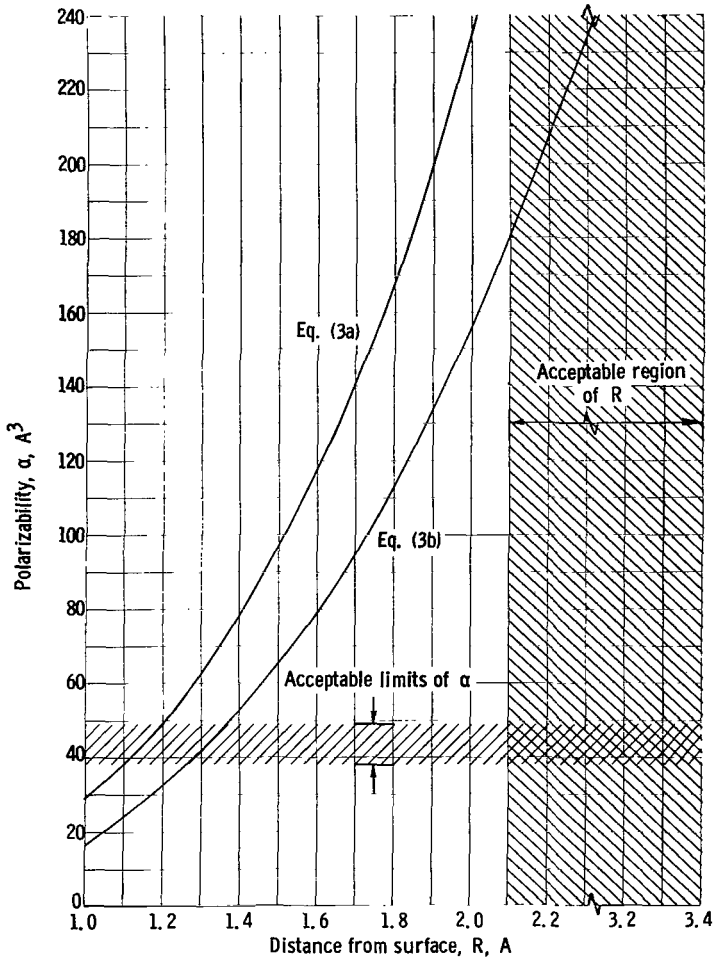

Figure 3. - Polarizability of adsorbed rubidium atom plotted against distance from tungsten substrate, based on two nonapplicable equations, (3a) and (3b). Rubidium heat of adsorption, 2.6 electron volt.

CONCLUDING REMARKS

As a result of the calculations performed, the theory of atom-metal interaction developed by Prosen and Sachs (ref. 7), equation (4) adequately explains the phenomenon of adsorption of alkali metal atoms on tungsten in the limit of zero coverage.

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 cesium adsorption there is only one reported value 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 26, 1964

APPENDIX A

SYMBOLS

a	constant
C	constant, ≈ 2.5
c	speed of light
e	electron charge
$\hbar$	Plank's constant divided by 2π
I	ionization potential of adsorbed atom, ev
k_m	$(3\pi^2\rho)^{1/3}$
m	electron rest mass
n	number of electrons of adsorbed atoms
n_o	conduction electron density of tungsten
R	distance from metal surface to nucleus of adsorbed atom
r	variable in appendix B
r_o	defined by eq. (B4)
r_s	radius of sphere in tungsten containing one conduction electron
V_A	attractive potential
V_R	repulsive potential
V_T	total potential
α	electronic polarizability of adsorbed atom
ν	resonance frequency of adsorbed atom, (ionization potential/Plank's constant)
ρ	number of conduction electrons per unit volume
φ	heat of adsorption in limit of zero coverage
χ	diamagnetic susceptibility

APPENDIX B

CORRECTION FACTOR FOR EFFECT OF REPULSIVE FORCE

The effect of adding a repulsive term

$$V_R = - \frac{a}{r^n} \tag{B1}$$

to an attractive potential

$$V_A = \frac{a}{r^m} \tag{B2}$$

to yield a total potential (with $n < m$)

$$V_T = V_A + V_R = a \left(- \frac{1}{r^n} + \frac{1}{r^m} \right) \tag{B3}$$

is equivalent to multiplying V_A by $1 - m/n$.

This can be seen from the differentiation of equation (B3)

$$\left(\frac{\partial V_T}{\partial r} \right)_{r=r_o} = 0 = \frac{an}{r^{n+1}} - \frac{am}{r^{m+1}} \tag{B4}$$

which yields

$$r_o^{n-m} = \frac{n}{m} \tag{B5}$$

Using this result in equation (B3) gives

$$V_T(r = r_o) = \frac{a}{r_o^m} - \frac{a}{r_o^{mn}}$$

$$= (V_A)_{r=r_o} \left(1 - \frac{m}{n} \right)$$

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