

VI. PHYSICAL ELECTRONICS AND SURFACE PHYSICS*

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A. DESORPTION KINETICS OF Cs⁺ FROM THE (100) FACE OF TUNGSTEN

1. Introduction

As a continuation of our studies of the alkali atom-refractory metal interaction, we have begun experimental measurements of desorption kinetics in the zero-coverage limit. The information from these experiments should complement the contact-potential difference measurements performed in this laboratory¹ and by the author elsewhere.² These experiments carried out on single-crystal specimens under extremely clean surface conditions gave rise to values of initial dipole moments different from those derived from measurements on polycrystalline specimens; dipole moments were also different for different crystal faces of the same material. By using single-crystal specimens and extremely clean surface techniques in desorption studies, we might expect to find differences in kinetics arising from differences in surface structure or residual gas contamination. Several authors³⁻⁶ have been successful in measuring both atomic and ionic desorption energies of cesium on tungsten surfaces. All but one, however, used polycrystalline samples, and none of them reported residual gas pressures better than 10^{-9} Torr. The measurements reported here are the desorption kinetics of cesium ions from the (100) face of tungsten between 900 and 1250°K.

2. Experimental Method

Our experiment combines a number of the techniques of modern surface studies.

1. Clean surface conditions, namely: ambient pressure $\sim 1 \times 10^{-10}$ Torr resulting in a low rate of surface contamination, and a pressure transient $< 1 \times 10^{-10}$ Torr on heating specimens to temperatures sufficiently high to desorb contaminants, thereby indicating that the concentration of such contaminants is $< 10^{-4}$ monolayer.

2. Oriented tungsten single crystals.

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3. Modulated molecular beam; this and other modulation techniques permit the use of sensitive detection and noise-averaging techniques.

A general analysis of the modulated molecular-beam technique as applied to surface studies has been published by Eberle in a previous report.⁷ Other authors³⁻⁸ have described its application to the present type of interaction. Briefly, the mean adsorption lifetime τ of a species on a surface at temperature $T^\circ\text{K}$ is given by the Arrhenius equation

$$\tau = \tau_0 \exp(\ell/kT), \quad (1)$$

where τ is the desorption energy of the species, and τ_0 a constant of the order of the vibration period of the species on the surface. We can calculate from the Saha-Langmuir equation the ratio of the ionic and atomic desorption probabilities

$$a = \frac{P_i}{P_a} = \frac{1}{2} \exp(\phi - V), \quad (2)$$

where ϕ is the work function of the surface, and V the ionization potential of the adsorbate. In our case $V = 3.89$ eV, and $\phi = 4.65$ eV, so ionic desorption predominates and we need only consider this single species. From the results of Eberle⁷ the ion current as a function of time t during beam-off conditions ($t = 0$ any time after the shutter has closed completely) is given by

$$I = I(0) \frac{\tau}{t_1} e^{-t/\tau} \left(e^{t_p/\tau} - 1 \right) \left(e^{t_1/\tau} - 1 \right) \left(1 - e^{-t_0/\tau} \right)^{-1}, \quad (3)$$

where t_0 is the chopping period, t_p the beam-on time, and t_1 the time during which the shutter is opening or closing.

For $t_0 > 5\tau$ and $t_1 < 5/\tau$ the equation is well approximated by

$$I = I(0) e^{-t/\tau}, \quad (4)$$

and for $t_1 < \tau/5$ but $t_0 < 5\tau$ by

$$I = I(0) e^{-t/\tau} \left(e^{t_p/\tau} - 1 \right) \left(1 - e^{-t_0/\tau} \right). \quad (5)$$

Values of τ may be obtained from the slopes of plots of \log (ion current) versus time when $t_0 > 5\tau$; for the case of $t_0 < 5\tau$ but $t_1 < \tau/5$, an approximate value of τ is chosen by inspection of recordings of ion current with time and Eq. 4 is used to calculate the zero current level; then, with a little iteration, a straight-line logarithmic plot may be obtained.

3. Apparatus

Figure VI-1 is a schematic diagram of the experimental tube. The tungsten single crystal, 6.25 mm in diameter and 2 mm thick, is mounted in the end of a tungsten cylinder, 1 cm long, and supported in the center of the tube by tungsten rods. Before mounting, the crystal was polished with carborundum paper to remove the damage produced by the electrical discharge machine used to cut it to shape, then lapped on glass with diamond paste, and finally electropolished in NaOH solution. A tungsten hairpin filament is mounted in the center of the cylinder to provide a source of radiation for indirect heating of the crystal or of electrons for electron bombardment heating. Indirect heating is used during measurements to maintain electrical isolation between heating and measuring circuits, and temperatures up to 1450°K can be maintained for long periods without risk of damage to the filament. For both indirect and electron

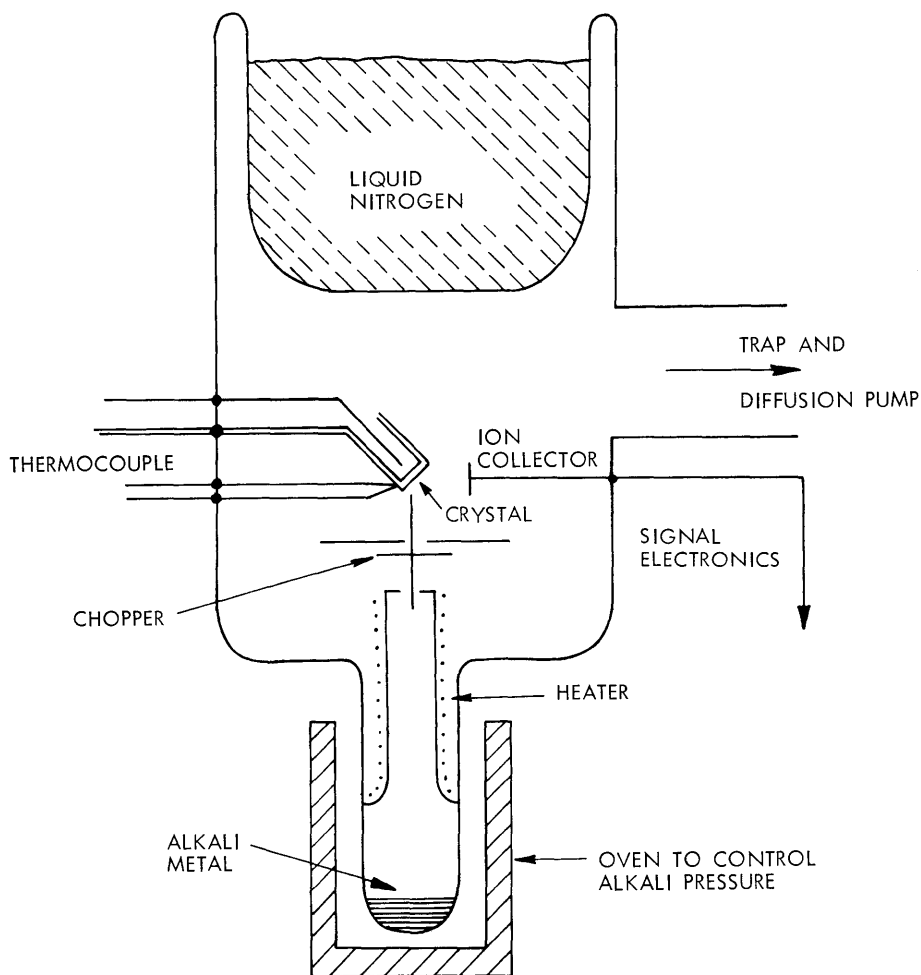


Fig. VI-1. Schematic of modulated molecular-beam apparatus.

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bombardment heating a Kepco DC power supply is used, for consideration of low noise and constant power in the former case and feedback control of the emission current in the latter. A tungsten 5% rhenium versus a tungsten 25% rhenium thermocouple is welded to the end of the tungsten cylinder for the measurement of the crystal temperature. The molecular-beam source consists of a reservoir that may be surrounded by a constant-temperature oil bath and a tube, heated to a temperature a little greater than the bath during experiments, onto the end of which is sealed a tungsten disc pierced by a 6 mm \times 0.25 mm slit. A molybdenum baffle, supported approximately 3 cm above the beam orifice, carries a second slit, 0.2 mm wide, aligned parallel to the first. The chopper blade moves below this slit.

Data from experiments on surfaces must always be accepted with some hesitation, since residual gas contamination can cause deviations from the pure system behavior even with ambient pressures in the low 10^{-10} Torr range, and pulsed molecular-beam experiments are no exception because the incorporation of choppers of the slotted-disc type involves vacuum-mounted bearings, motors or rotary motion feedthroughs, all of

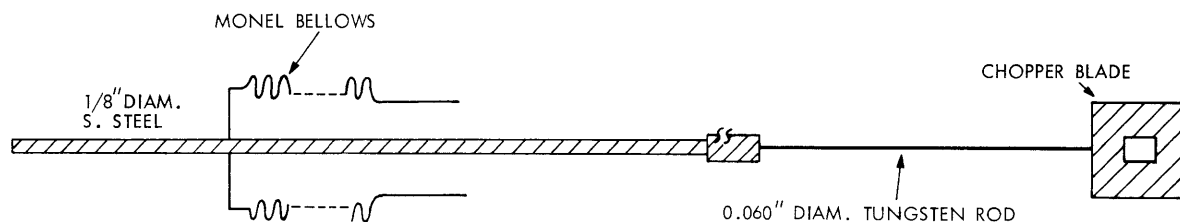


Fig. VI-2. Vibrating beam chopper.

which are sources of additional background gas. In this experiment beam modulation is achieved by using a chopper based on a vibrating cantilever. The geometry of the chopper (Fig. VI-2) allows 3 chopping speeds separated by approximately 2 octaves. The bellows serve only to permit the chopper blade to be positioned correctly and are not a part of the vibrating system. The rod is clamped in position where it passes through the bellows, and the free end is driven with a loudspeaker type of vibrator at a resonant frequency of the rod, exciting vibrations in the rod. The compound structure of the rod has two natural modes capable of usefully large amplitudes, and the frequencies of these modes are approximately 75 and 170 Hz. The chopper blade may be positioned so that the "beam-on" condition occurs either once or twice each period. Four chopping speeds are therefore available, although 2 differ only a little. Shutter

functions compare favorably with those of rotating-disc shutters for our application.

Vacuum-distilled cesium was introduced into the reservoir from a breakable glass capsule when ultrahigh vacuum had been achieved. Slow distillation of the cesium from its position during bakeout to the reservoir further increases its purity. When measurements were not in progress the reservoir was continuously pumped, a ball and socket valve was used to close the connection when the reservoir was heated. The dewar in the top of the tube was filled with liquid nitrogen during measurements to reduce the pressure of cesium in the tube.

The bakeable mercury-in-glass diffusion pump system used to evacuate the tube has been described by Bergman in an earlier report.⁹ The ultimate pressure was improved by baking out at a higher temperature and by trap-dropping techniques. Following bakeout the crystal was degassed at temperatures between 2400°K and 2800°K for more than 200 hours. During these periods the temperature was raised at intervals to 3000°K for approximately 1 minute at a time to remove carbon from the surface. The tantalum strip ion collector was also degassed at high temperatures but for shorter times. The empty reservoir and beam tube were heated to temperatures greater than those employed during measurements until they produced no significant increase of the background pressure. Outgassing was considered to be complete when the crystal could be flashed to a

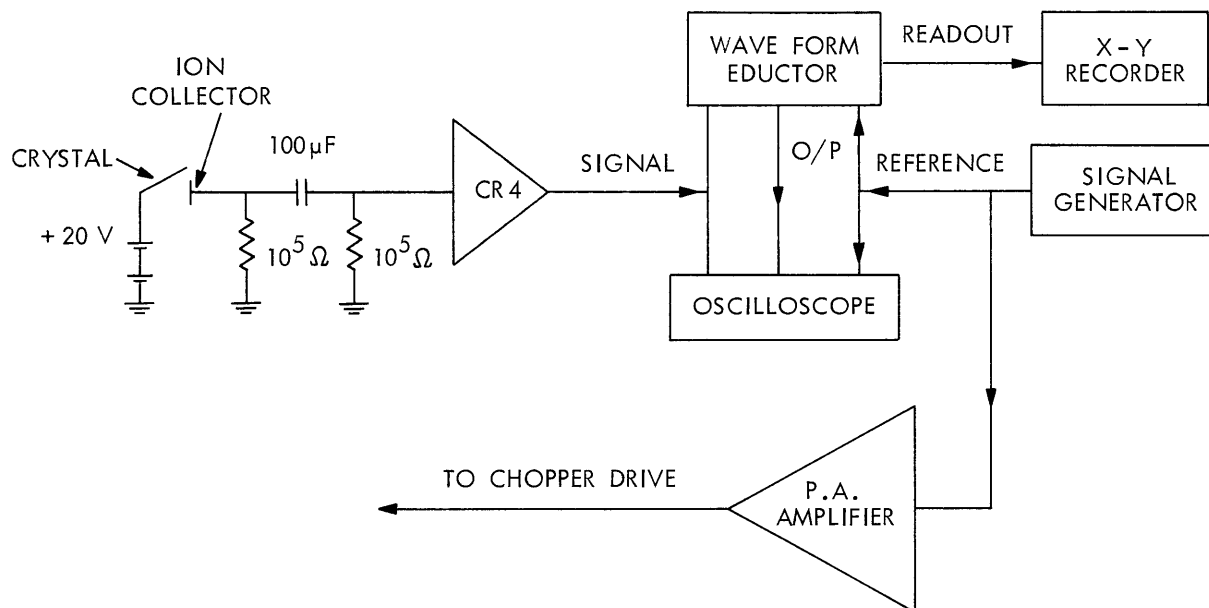


Fig. VI-3. Measurement circuit.

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high temperature without a pressure transient of greater than 1×10^{-10} Torr. At this stage the cesium capsule was broken and cesium distilled into the reservoir.

The circuit used for ion current measurements is shown in Fig. VI-3. Following amplification by a P. A. R. CR4 wideband amplifier, the signal is input to the P. A. R. waveform eductor which can be read into an X-Y recorder. The waveform eductor is a multichannel signal-averaging device that may be triggered internally or externally. In our application the source used to drive the vibrator is used as an external trigger. Calibration of the signal generator is carried out at both of the driving frequencies used by counting the number of cycles generated in 1000 sec measured by an accurate time-piece.

4. Measurement Procedure

Measurements proceeded as follows. The crystal and ion collector were flashed to a high temperature with the crystal then repeatedly heated to $\sim 2600^\circ\text{K}$ at 5- or 10-min intervals until the pressure transient was less than 1×10^{-10} Torr. This ensured that the surface was clean at the start of the experiment. Liquid nitrogen was then placed in the cesium dumping dewar, the crystal was maintained at 1400°K by indirect heating, and the oil bath power supply connected. After the bath temperature had reached its programmed temperature, 100°C - 140°C , the crystal was flashed to a high temperature and then returned to 1400°K . At this stage the pressure was $< 5 \times 10^{-10}$ Torr and suitable conditions for measurements existed. The chopper was set in motion and the measurement circuit connected.

Ion current-time curves were recorded for different temperatures. After a change in power supplied to the crystal, the waveform eductor was set in the sampling mode until the temperature reached a steady value. The stored waveform was then read out and the thermocouple e. m. f. noted.

5. Results and Discussion

Mean lifetime measurements were obtained in the temperature range 900°K - 1250°K . Figure VI-4 shows the Arrhenius plot of these data, and from the slope and intercept of the plot we deduce the following values:

$$\text{Cesium ion desorption energy} = 2.06 \pm .01 \text{ eV}$$

$$\text{Pre-exponential} = \tau_0 = 1.24 \pm .14 \times 10^{-13} \text{ sec.}$$

Values of τ were determined within $\pm 10\%$ in the middle of the range and with about half this precision at the extremes. Thermocouple e. m. f.'s were determined to $\pm 1\%$. Life tests on this thermocouple have shown no drift to within $\pm 2\%$.¹⁰ A batch calibration was

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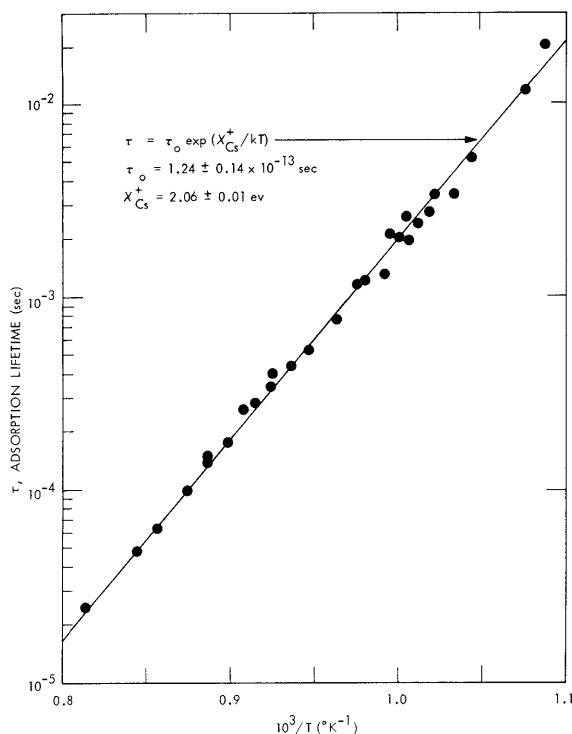


Fig. VI-4. Desorption of Cs^+ from (100) W.

used to convert e.m.f. to temperature. The temperature was thus determined with an accuracy similar to that obtained when using a calibrated window with an evaporation shield and a specimen with a black-body hole, that is, approximately $\pm 2\%$.

To determine whether the cesium on the surface could have migrated off the front face of the crystal before desorption, the mean number of lattice spacings moved before desorption was estimated from equations in published material.¹¹ This number was found to be 3000 at 900°K and approximately one-tenth for the highest temperature. This represents a distance of the order of 1 micron, which is negligible in our case. Another source of error could be a change in the desorption kinetics resulting from a finite cesium surface coverage, and to investigate this possibility, the number of atoms incident on the surface per second was calculated from a measurement of the DC ion current. This current gave rise to a maximum instantaneous surface coverage of less than 10^{-3} monolayer over the area on which the beam was incident at the longest lifetimes.

Table VI-1 shows the parameters measured in this study, those of Scheer and Fine³ for polycrystalline tungsten and those from Koenig and Pigford's⁴ cesium diode study of the (100) face of tungsten.

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Table VI-1. Parameters.

	<u>Present</u>	<u>Scheer and Fine</u> ³	<u>Koenig and Pigford</u> ⁴
Energy (eV)	2.06 ± .01	2.04 ± .06	2.05 ± .05
Pre-exponential	1.24 ± .14 × 10 ⁻¹³	11 ± 6 × 10 ⁻¹³	1.5 ± 0.5 × 10 ⁻¹³

The agreement with Koenig is extremely close and well within the experimental error. Agreement with Scheer and Fine is also close, if one considers the different natures of the surfaces concerned. The latter agreement may indicate that the polycrystalline surface was largely (100) or that the desorption is insensitive to the crystallographic nature of the surface. It also indicates that Scheer and Fine may have been able to make measurements soon enough after surface cleaning to avoid contamination effects.

If we consider an electrostatic image model of the cesium surface interaction, then for a particle charge q (Coulombs) distant r (meters) from the surface, the desorption energy can be expressed as³

$$\ell^+ = \frac{q^2}{16\pi\epsilon_0 E_0 M} \text{ eV} \quad (6)$$

and the dipole moment as²

$$M = qr \quad \text{Coulomb meters.} \quad (7)$$

If our measured values for desorption energy and the mean of the values of Lee² (2.75×10^{-29} Coulomb meters) and Fehrs¹ (2.52×10^{-29} Coulomb meters) are used for the initial dipole moment of cesium on W (100), the simultaneous solution of Eqs. 6 and 7 gives values of $q = 0.98 e$ and $r = 1.68 \text{ \AA}$. These figures indicate a closer agreement with the classical picture than with the quantum-mechanical calculations of Gadzuk.¹²

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B. CONTACT-POTENTIAL MEASUREMENTS OF THE ADSORPTION OF CESIUM AND POTASSIUM ON (100) TUNGSTEN

1. Introduction

The purpose of this report is to summarize briefly the results obtained from studies of work-function changes resulting from the adsorption of Cs and K on a (100) W surface. All runs were made with the crystal at 300°K, with the exception of a set of Cs runs which will also be mentioned. With minor exceptions, the measurements utilized an apparatus unchanged from that reported previously.¹ One difference is that a more massive 1/4 in. diam. (100) W target, heated by electron bombardment, has replaced the thin (1 mil), resistively heated Ta ribbon targets. Also, the alkali ion-gun sources have been modified slightly, because of the change in target geometry.

2. Results

An interesting effect seen in studies of Cs on (100) W was a distortion of the true Cs density scale by migration of Cs off the surface. In an early set of runs, insufficient time was allowed for the relatively massive W crystal to cool following flash cleaning before the deposition of Cs. In this case, a large surface migration effect might be expected, and it was seen, in that a plot of work-function change vs apparent Cs density yielded unrealistically high densities (Fig. VI-5). Despite the distortion of the density scale, these results allowed us to measure both the minimum and monolayer work functions for Cs on (100) W. In another set of runs, the crystal was always allowed to cool to 300°K before deposition of Cs. Below a surface density of $\sim 9 \times 10^{13} \text{ cm}^{-2}$, the work-function change coverage plot showed no large surface migration effects. Above this coverage, however, migration effects began to be seen, as evidenced by a growing nonreproducibility and time dependence of the data. This surface migration effect at 300°K is interesting, since it was not seen in our studies of K on (100) W or in our earlier studies of Cs, K, and Na on (110) Ta.²

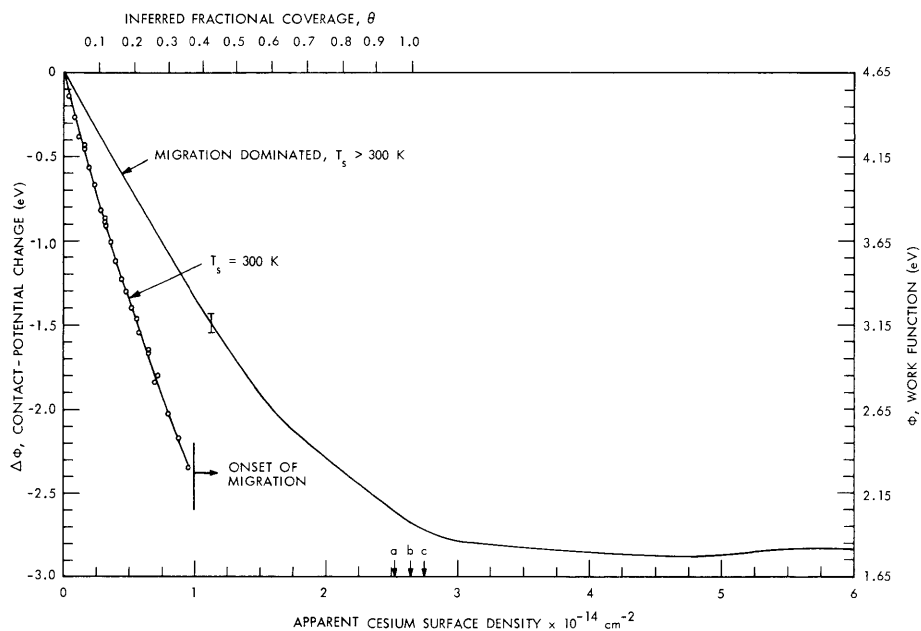


Fig. VI-5. Results for Cs on (100) W. $p < 1 \times 10^{-10}$ Torr, apparent target area 0.316 cm^2 .
 a. Monolayer coverage for a 1:4 packing ratio between adsorbate and substrate;
 b. Monolayer coverage point inferred from data of Lee;
 c. Packing density for a (100) Cs surface.

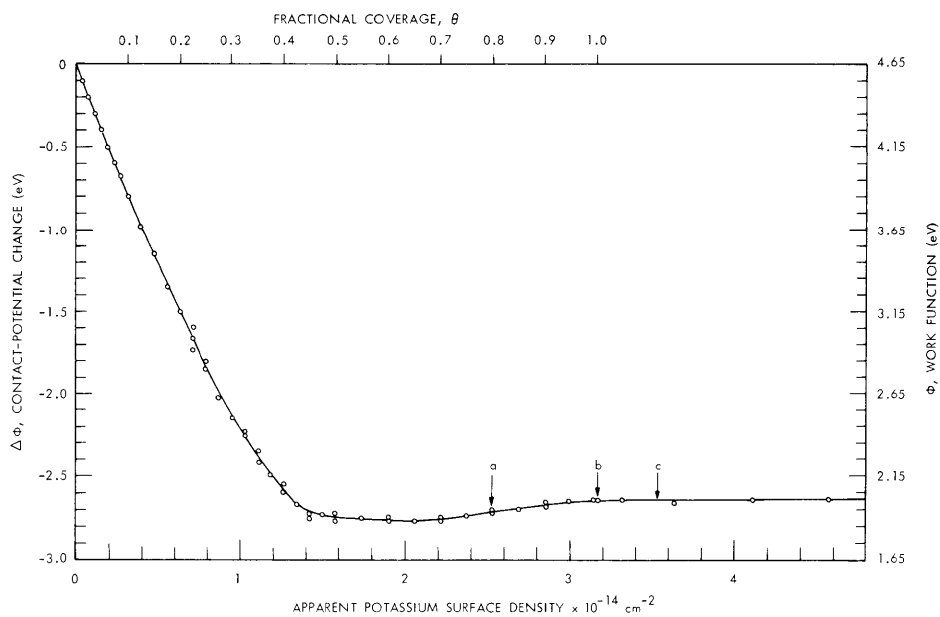


Fig. VI-6. Results for K on (100) W. $p < 1 \times 10^{-10}$ Torr, apparent target area 0.316 cm^2 , $T_s = 300^\circ\text{K}$.
 a. Monolayer coverage for a 1:4 packing ratio between adsorbate and substrate;
 b. Defined monolayer coverage;
 c. Packing density for a (100) K surface.

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The slope of the nondistorted portion of the 300°K work-function coverage data yielded a near-zero coverage dipole moment of 15.24D. This corresponds to a fully ionic dipole half-length of 1.56 Å. If a bare surface work function of 4.65 eV is assumed for (100) W,³ the minimum work function, upon cesiation, is 1.77 eV, while the monolayer value is 1.82 eV.

Studies of K on (100) W at 300°K showed no evidence of surface migration so it was possible to obtain an undistorted work-function density plot over the entire coverage range (Fig. VI-6). These results yielded a near-zero coverage dipole moment of 13.45D, corresponding to a fully ionic dipole half-length of 1.38 Å. Upon potassium adsorption, a minimum work function of 1.88 eV and a monolayer work function of 2.01 eV were obtained. At monolayer coverage, the K surface density was $3.16 \times 10^{14} \text{ cm}^{-2}$. It is interesting to note that this density is considerably larger than that predicted by packing of K only into available surface sites ($\sim 2.5 \times 10^{14} \text{ cm}^{-2}$),⁴ and is nearer the value of the density expected for a (100) face of bulk K ($\sim 3.5 \times 10^{14} \text{ cm}^{-2}$).

3. Discussion of Results

The minimum and monolayer work functions of 1.77 eV and 1.82 eV, respectively, found in the present study of Cs on (100) W, agree well with the corresponding values of 1.795 eV and 1.82 eV found by Lee⁵ in his study of Cs on (100) W. Since Lee could not measure absolute Cs densities, our low-coverage Cs data provide a means of calibrating Lee's data to an absolute density scale. When this is done, a monolayer density of $2.66 \times 10^{14} \text{ cm}^{-2}$ results. This value is nearly midway between the density for packing only into surface sites ($\sim 2.5 \times 10^{14} \text{ cm}^{-2}$), and the density of a (100) Cs surface ($2.75 \times 10^{14} \text{ cm}^{-2}$). This apparent tendency for Cs and K to assume monolayer packing densities near those expected for (100) Cs and (100) K surfaces, respectively, confirms a result seen in our earlier studies of Cs, K, and Na on (110) Ta. In these studies, monolayer densities were nearer the values expected for (110) surfaces of the bulk alkali than the values predicted by packing into available surface sites.

Comparison of the present data with our (110) Ta produces additional interesting observations. First, the zero-coverage dipole half-lengths for adsorption of Cs on K on (100) Ta were 1.57 Å and 1.38 Å, respectively, compared with the values of 1.56 Å and 1.38 Å found for Cs and K, respectively, on (100) W. Second, the minimum work functions for Cs and K on (110) Ta were 1.72 eV and 1.88 eV, respectively, compared with 1.77 eV and 1.88 eV for Cs and K, respectively, on (100) W. Since the bare surface work function of (110) Ta (4.9 eV) is higher than that of the (100) W (4.65 eV), the agreement found in these dipole moments and work-function minima is surprising. Finally, the monolayer work functions for Cs and K on (100) W (1.82 eV and 2.01 eV, respectively) are, as expected, lower than those found for Cs and K on (110) Ta (1.96 eV and 2.22 eV, respectively).

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