Mean Adsorption Lifetime of Rb on Etched Tungsten Single Crystals: Neutrals*

F. L. HUGHES

Physics Department, Syracuse University, Syracuse, New York

(Received July 14, 1958)

The mean adsorption lifetime has been measured for the fraction of adsorbed Rb which was desorbed as neutral atoms from an etched W surface. The lifetime was found to be greatly different from that obtained in the case of Rb ions. Experimental values have been found to be consistent with a theoretical model which assumes that, in a surface ionization process, the adsorbed particles may occupy either of two discrete states with distinctly different types of binding.

I. INTRODUCTION

N the surface ionization process, some of the adsorbed particles are desorbed as ions and some as neutral atoms. For steady-state conditions where desorption is balanced by additional incoming particles, the ratio of desorbed ion current density to desorbed atom current density is given by $I_i/I_a = (\omega_i/\omega_a) \exp[e(\phi - I)/kT]^{1}$. The ratio of weight factors, ω_i/ω_a , is $\frac{1}{2}$ for alkali metals, ϕ is the surface electron work function, and I is the alkali ionization potential. Past work with the alkali metal-tungsten system, including experimental verification of the Langmuir-Saha equation above, was consistent with the hypothesis that there are both an ionic state and an atomic state of the adsorbed particle. This view was strongly supported by Taylor's² measurements which gave a different desorption rate for ions and atoms. Gurney,3 however, has given theoretical arguments which imply that, in the adsorbed state, the alkali and surface interact in such a way as to make ion and atom indistinguishable. The relative probability of ion/atom desorption was assumed to be determined by relative valence electron probability density inside/ outside the surface barrier. This view implies that experimental measurements of the mean adsorption lifetime for particles desorbed as ions would be the same as that measured for particles desorbed as neutral atoms.

The present work was designed to check this prediction. The mean desorption lifetime on "essentially clean," etched W crystals has been measured for Rb which was desorbed as Rb neutral atoms.⁴ This was accomplished by using a second surface ionization filament to detect the neutral atoms from the surface under examination.

II. EXPERIMENTAL

Most of the apparatus and methods have been described previously.⁴ The major modification is shown

* Supported by Office of Ordnance Research.

¹ I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. (London) A107, 61 (1925).

in Fig. 1. A chopped Rb atomic beam impinged upon the etched tungsten filament, W_1 . Neutral Rb atoms which were desorbed were permitted to drift with thermal energy to the second filament, W_2 , where they were adsorbed a second time. The desorbed ions from the second filament were focused and accelerated by the electrode, A. After passing through A, the ion pulse was amplified by the secondary emission multiplier. The signal was passed into conventional electronic amplifiers and displayed on an oscilloscope in the same manner as for the ion pulse work which was previously described.⁴ With the exception of a small Boltzman "tail," due to the thermal drift in part of the trajectory, the oscilloscope trace of the neutral pulse had the same appearance as that shown for the ion pulse.

1. Electronics

For Rb on etched tungsten ($\phi = 5.25$ v), the ion/atom current density ratio is $\approx 2.5 \times 10^4$ at 1200° K. In order to keep the surface coverage low, it was necessary to operate at about the same beam intensity as was used for the ion work.⁵ In addition, the geometrical losses of neutral atom current between W_1 and W_2 was of the order of 103. The additional gain required over that required by the ion work was thus of the order of 10^6 .

The additional amplification required was obtained



FIG. 1. Apparatus for measurement of neutral Rb adsorption lifetime.

⁵ In this measurement, the coverage was about 10¹¹ atoms/cm². Rb-Rb interaction effects are expected to be much less than the experimental error.

² J. B. Taylor and I. Langmuir, Phys. Rev. 44, 423 (1933). ³ R. W. Gurney, Phys. Rev. 47, 479 (1935). ⁴ The crystal preparation, surface cleanliness measurements, and ion lifetime measurements have been discussed by F. L. Hughes and H. Levinstein, preceding paper [Phys. Rev. 113, 1029 (1959)].



FIG. 2. Rb⁺ and Rb⁰ adsorption lifetime versus 1/T, for Rb on clean, etched W.

with the secondary emission multiplier. The multiplier⁶ was a half-scale Allen⁷ type with Ag-Mg alloy dynodes. Since nothing was known about the effect of mercury on this alloy, cold traps were used constantly to prevent the entrance of mercury pump vapor into the detector chamber. The electrodes from W_2 , through A, to the first dynode, D, were arranged by use of electrostatic plots made on conducting paper. The plots indicated that with the arrangement and the voltages shown on Fig. 1, the structure focused the ions from W_2 to the proper part of the first dynode.

The dynode power supply was a 2-5 kv rf supply⁸ fed from a separate regulated 300-volt dc supply.9 At 3 kv the rf ripple was of the order of millivolts. It should be noted that for these short pulses, the distortion due to variation in multiplier gain and electron transit time will be negligible for even a conventional 60-cycle supply with a few hundredths of a percent ripple. This results from the fact that the pulse is essentially completed in a small portion of the 60-cycle ripple period.

2. Neutral Atom Data

The procedure for obtaining Rb atom adsorption lifetimes was the same as for the ion work. Figure 2 shows a plot of mean life versus 1/T for the neutrals. The Rb⁺ mean life is shown for comparison. The percent experimental error is about the same as for the ion work. The parameter values were $Q_a = 2.60 \pm 0.1$ ev and $\tau_a^0 = 2.5 \times 10^{-13}$ sec.

3. Contamination

No detailed measurements were made of the lifetime as a function of contamination; however, the behavior was qualitatively the same as that found for the ion

- J. S. Allen, Rev. Sci. Instr. 18, 739 (1947).
- D. Marple, dissertation, Syracuse University (unpublished).
 W. C. Elmore and M. Sands, *Electronics* (McGraw-Hill Book
- Company, Inc., New York, 1949), p. 373.

work. The data of Fig. 2 are clean within the meaning previously defined.⁴

4. Transit Time Effects

Under the experimental conditions, the neutrals drift with thermal energies $(T \approx 1400^{\circ} \text{K})$ from W_1 to W_2 (Fig. 1). Since particles have a Boltzman velocity distribution,¹⁰ the shape of the neutral pulse will be affected by the temperature of W_1 and the W_1-W_2 distance (≈ 3 mm). The kinetic theory velocity spread for these conditions will cause a difference of approximately 5×10^{-6} sec between the slowest atom and the fastest atom transit times. This is not expected to affect lifetime measurements in the range of 10^{-4} sec. For lifetimes shorter than about 5×10^{-5} sec, however, the effect will be important.

The time delay caused by adsorption on W_2 can be reduced to any desired level by operating W_2 at such a high temperature that the ion adsorption lifetime is negligible. The transit time through the photomultiplier from W_2 is less than 5×10^{-7} sec and is constant for all neutrals in the pulse.

III. THEORETICAL

Figure 3 shows the theoretical model. It is similar to that used by Varnerin¹¹ and Hagstrum.¹² If the ionization energy, I, is added to a Rb atom at a distance far from the surface, the subsystem (Rb⁺ and its electron) is raised to the level, A. If the electron is removed and placed in the Fermi "sea" of the metal, then the ion level will drop by an energy, ϕ , and thus the ion level will be at C. The ion is moved toward the surface, and the ion-surface potential will be that of curve C. Since there are a number of unfilled levels in the metal, however, the electron may also be placed in a number



FIG. 3. Energy scheme for Rb on W as function of particle-surface separation. Inset shows the kinetic diagram.

- ¹⁰ N. I. Ionov, J. Exptl. Theoret. Phys. U.S.S.R. 18, 96 (1948).
 ¹¹ L. J. Varnerin, Phys. Rev. 91, 859 (1953).
 ¹² H. D. Hagstrum, Phys. Rev. 96, 336 (1954).

⁶ Obtained from National Company, Inc. The manufacturer specified a gain of 10^6 when used for 3.0-kv K^+ ions.

of discrete states ranging from the vacuum level down to ϕ electron volts below the vacuum level. This will produce a band of ion states ranging from curve A to curve C. Curve B represents one of these states between the two extremes.

The atom level represents the potential as an atom moves closer to the surface. Judging from the magnitude of the experimental neutral desorption energy, the binding appears to be due to exchange forces.

Transitions between ion and atom states are possible at points where the potential curves cross. Very little is known about the potential shapes and relative positions of the potential minima. For the potentials shown in Fig. 3, there are so many crossing points that there is access to and from any ion-atom level.

The inset in Fig. 3 shows the diagram in terms of transition and desorption probabilities/second. The transitions P_1 and P_2 are included to account for the possibility of ion-atom interchange. With initial ion and atom surface concentrations n_i and n_a , respectively, the time variation in these concentrations is given by

$$\dot{n} = -(P_a + P_2)n_a + P_1n_i,
\dot{n}_i = P_2n_a - (P + P_1)n_i.$$
(1)

Owing to the number of parameters involved, the general solutions of Eq. (1) cannot be used. It is possible, however, to show that the equations are consistent with the experimental situation. The following boundary conditions were applied:

(a) Assume that the ion and atom pulse time decay is a true exponential and that the lifetime variation with 1/T is a true exponential. Within experimental error this assumption is valid. However, semilogarithmic plots covering many decades are usually necessary in order to be certain

(b) Assume that the Langmuir-Saha equation is valid under pulse conditions. This assumption will be valid if the particles have time to come into quasi-equilibrium with the lattice.⁴

From (b), we have

$$I_i/I_a = P_i n_i/P_a n = (\omega_i/\omega_a) \exp[e(\phi - I)/kT], \qquad (2)$$

and

$$n_i = (\omega_i P_a / \omega_a P_i) \exp[e(\phi - I) / kT] n_a = \beta(T) n_a.$$
(3)

Equation (1) becomes

$$\dot{n}_a = -(P_a + P_2 - P_1\beta)n_a,$$

$$\dot{n}_i = -(P_i - P_2/\beta + P_1)n_i.$$

(4)

The experimental desorption probabilities will be given by

$$P_{a}(\text{experimental}) = P_{a} + P_{2} - P_{1}\beta,$$

$$P_{i}(\text{experimental}) = P_{i} - P_{2}/\beta + P_{1}.$$
(5)

Equation (5) satisfies the part of condition (a), concerning exponential pulse decay. However, the condition on the temperature dependence of lifetime can be satisfied only if (1) P_1 , $P_2 \ll P_i$, P_a ; or if (2) $P_2/P_1 = \beta$. Since P_1 and P_2 represent electronic transitions which are expected to occur in $\approx 10^{-15}$ sec, the first possibility is unlikely. If the desorption probabilities are written in the form

 $P_{i,a} = (\tau_{i,a}^{0})^{-1} \exp(-Q_{i,a}/kT)$, and $P_2/P_1 = \beta$, (6) then the experimental boundary conditions are satisfied. Since $\Delta Q = \phi - I + Q_i - Q_a$, where ϕ and I are now expressed in electron volts, Eq. (3) can be written

$$\boldsymbol{\beta} = (\omega_i \tau_i^0 / \omega_a \tau_a^0) \exp(\Delta Q / kT) = P_2 / P_1. \tag{7}$$

Equation (7) has the form to be expected from statistical mechanics. The pre-exponential factor should represent the ratio of the densities of the vibrational states in the ion and atom levels. Becker's¹³ calculation for the ratio, n_i/n_a , under steady-state conditions produced a term resembling β .

1. Effects of Retarding Field

As is shown in Fig. 1, a retarding field was applied to W_1 to suppress ion evaporation. Originally, it was intended to operate W_1 with a low accelerating field. Under those conditions, however, it was found difficult to prevent stray ions from entering the space of C_2 . The following considerations show that the neutrallifetime results will not depend on field polarity.

The effect on the ion-surface potential depth caused by an applied exterior field will be of the form of a Schottky term, $e(eE)^{\frac{1}{2}}$, since the potential is primarily an image potential. From thermionic electron emission from the etched surface, the term was found to be less than 0.01 ev, with a $C_1 - W_1$ potential difference of 50 volts. The field effect on the neutral atom-surface potential should be much less.

Therefore, the energy diagram will be the same as before. Equations (3) and (4a) are still valid and the result is $P_a(\text{experimental}) = P_a$. The ion state population thus furnishes a reservoir of particles but does not affect the neutral evaporation rate.

IV. CONCLUSION

The mean desorption lifetime of Rb has been measured for Rb desorbed as neutral atoms from "essentially clean," etched W. The values were different from the lifetime measured for Rb desorbed as ions.

The data have been found to be consistent with a model which assumes that, in surface ionization, ion and atom states are discrete and different. The ion state is primarily due to image forces. The atomic state appears to be due to exchange forces.

V. ACKNOWLEDGMENTS

The author is indebted to Professor H. W. Berry and Professor H. Levinstein for several helpful discussions. Mr. S. Borrello very kindly assisted with some of the apparatus construction. Mr. R. Buies assisted with the diagrams.

¹³ J. A. Becker, Ann. N. Y. Acad. Sci. 58, 723 (1954).