

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

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Using an interrupted atomic beam technique, the mean adsorption lifetime, τ_i , has been measured for Rb ions adsorbed on an "essentially clean," etched tungsten surface. Etching produced a homogeneous surface with a uniform work function. An estimated 90% of the surface consisted of microcrystal facets of the same crystallographic plane. The maximum Rb concentration was about 10^{10} atoms/cm².

The data may be represented by the equation $\tau_i = \tau_i^0 \exp(Q_i/kT)$, in the region $1100 < T < 1300^\circ\text{K}$. The weakly temperature-dependent term τ_i^0 appears to be affected by the shape, near the minima, of the ionic potential barrier of height Q_i .

Lifetime measurements indicated that τ_i^0 and Q_i are strongly affected by the physical state of the metal and by the type and degree of contamination. It was found that τ_i^0 as well as Q_i must be used in characterizing "chemical" adsorption processes.

I. INTRODUCTION

THE surface ionization process¹ may be described in the following way. An atom, adsorbed on a clean metal surface, may lose a valence electron to one of the higher Fermi levels of the metal. The probability for ionization is high if the electron work function of the metal is equal to or greater than the ionization potential of the free atom. At sufficiently high surface temperatures, the adsorbed particle migrates about on the surface and may eventually evaporate as a positive ion. Since the ions can be readily detected, the process provides a very direct method of observing the desorption rate. From the variation of the desorption rate with temperature, surface conditions, and contamination, one can obtain information concerning the atom-metal interaction.

The desorption rate can be expressed as $\dot{n}_i = -n_i P_i$, where n_i is the surface concentration of atoms/cm², and P_i is the evaporation or desorption probability/second. For high values of n_i the desorption probability depends on n_i and the measured rates will not only be characteristic of the atom-metal binding but will include effects due to the atom-atom interaction. For low values of n_i therefore, the value of P_i is the significant term.

Early values of P_i for alkali metals adsorbed on tungsten,^{2,3} were obtained by measuring \dot{n}_i and n_i separately. Several years ago, a technique was described⁴⁻⁶ which makes possible the direct measurement of P_i . In this method, a periodically interrupted atomic beam provides short bursts of atoms which are allowed to become adsorbed on a metal, usually in the form of a wire. The atoms remain on the wire for a period of time. Some of them evaporate as ions and are measured electrically. For suitable boundary conditions, the ions

resulting from an individual pulse of atoms will produce a decaying exponential ion current of the form $\exp(-P_i t)$. In analogy to other physical processes with similar behavior, it was natural to define the mean life of the adsorbed particles as $\tau_i = 1/P_i$.

In the work to be described, a rotating, slotted disk was used to interrupt a Rb atomic beam which struck a specially treated tungsten filament. The mean life of the adsorbed Rb⁺ was measured as a function of temperature for various surface conditions and with several kinds and amounts of foreign atom contamination.

The reasons for venturing into such an overworked field were twofold. (1) The divergent results^{5,6} obtained by different investigators with this method for the surface ionization of potassium indicated that some significant parameters had been ignored; it seemed worthwhile to investigate the effects produced by varying some of the obvious parameters such as contamination and surface crystal structure. (2) Recent work with molecular beams has required an extremely sensitive detection system; for beams which can be detected by the surface ionization process, the "chopped" beam method, with its high signal-to-noise ratio, appears to have great advantages over the constant-beam detection method.

II. EXPERIMENTAL (PART A)

1. Apparatus

Figure 1 shows the experimental tube. The oven and collector chambers were separately pumped with large, three-stage, mercury diffusion pumps. Two liquid nitrogen-cooled traps were inserted in each pump line.

The Pyrex oven contained Rb which had been triply vacuum distilled from C.P. grade metal. The oven was heated by passing current through a spiral of colloidal silver paste connecting electrodes at each end of the oven. At the operating temperature, enough Rb was produced to coat the walls of the oven chamber with a monolayer of Rb every second. The chamber thus served as a getter pump which reduced the oxygen

* Supported by the Office of Ordnance Research.

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

² I. Langmuir, Phys. Rev. **22**, 357 (1923).

³ J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933).

⁴ I. L. Kofsky and H. Levinstein, Phys. Rev. **74**, 500 (1948).

⁵ F. Knauer, Z. Physik **125**, 278 (1948).

⁶ C. B. Starodubtsev, J. Exptl. Theoret. Phys. U.S.S.R. **19**, 216 (1949).

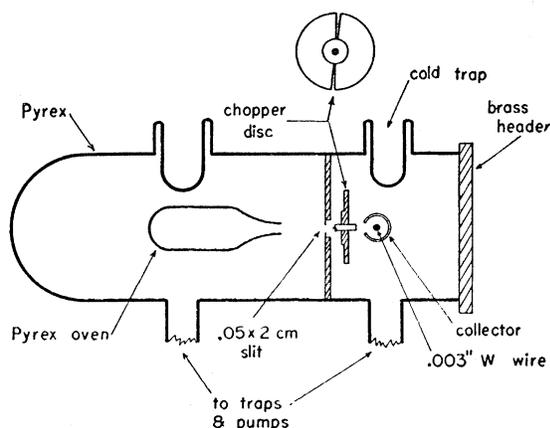


FIG. 1. Rb atomic beam, vacuum system.

content of the residual gas to a low value. Because of the high Rb concentration in the oven chamber, the baffle slit acted as virtual source for the atomic beam.

After passing through the baffle slit, the Rb beam encountered a slotted disk "chopper" which was driven by a small induction motor. The chopper served as a periodic shutter, passing a low-duty-cycle beam. Since no commercially made motor seemed suitable for vacuum work, a specially designed motor was built which operated at high current and low voltage (3 amp, 0.2 volt, 250 cycles/sec). It was possible to use only 30 turns of field coil winding with Teflon insulation. The rotor was supported by "Miniature Precision" ball bearings which were lubricated by MoS_2 . The speed could be varied between 3000 and 10 000 rpm.

The pulsed beam emerging from the chopper struck a hot 0.003-in. diameter tungsten filament and the positive ions produced at the wire were drawn to the collector. The cylindrical collector had electrical guard rings at each end and was mounted co-axially with the tungsten wire. A small hole in the collector permitted the observation of the wire with a disappearing-filament-type optical pyrometer.

The optical pyrometer was checked against a cavity blackbody and Pt-Pt:Rh thermocouple for the temperature range of interest. Tungsten brightness temperatures were converted to true temperature by tables prepared by Forsythe.⁷ End loss effects were negligible.

Ion collection was made at 45 volts. Data taken by Zemel⁸ indicated that the field was too low to affect the desorption process. The collector current was passed to a preamplifier, a Hewlett-Packard Model 450A wide-band amplifier, and thence to a Tektronix Model 513 oscilloscope. Ion current *versus* time data were taken with a Polaroid record camera. The over-all gain was such that a pulse containing 10^6 Rb atoms produced a one-volt

peak at the oscilloscope input. Several orders of magnitude could have been gained by using secondary emission multiplier techniques.

Using the amplifiers, the shortest ion pulse obtainable was analyzed with a General Radio Model 736A wave analyzer. The significant frequency components were well within the distortion-free region of the amplifiers as determined by frequency and amplitude response and phase-shift measurements. Since all of the available information about the ion desorption was contained in the shape of the ion current *versus* time curves, an additional check was made for amplifier distortion. Using a spike pulse through an RC network, the decay characteristics of the ion current were simulated. The decay times were varied over the range of measured ion-current decay times (adsorption lifetimes) with no observable distortion due to amplifiers.

III. DATA

Figure 2 shows the oscilloscope traces for ion current *versus* time at various wire temperatures. Note that the Polaroid print presents time increasing to the left. The traces are all on the same time base, of about 10^{-4} sec/division, and the amplifier gain increases from the top to the bottom trace. Time base measurements were made with an audio-oscillator which was checked against a standard 2000-vibration/sec tuning fork.

The first trace of Fig. 2 was taken at such a high tungsten temperature that the lifetime was negligible, and thus it represented the shape of the chopped atomic beam pulse. If this pulse has a distribution in time of $f(t)$ atoms/cm² sec, then the ion current will be given

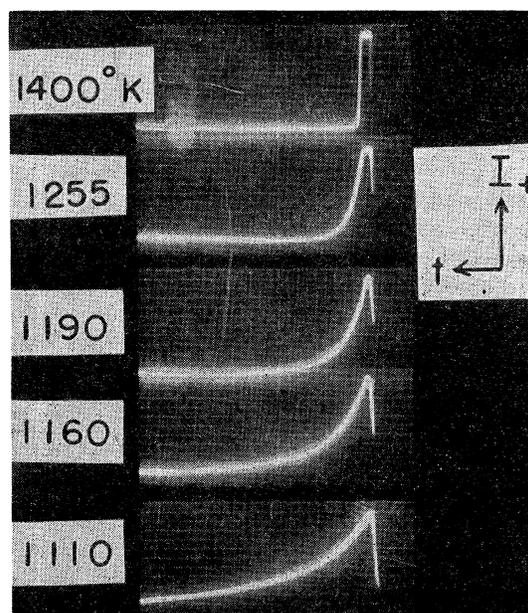


FIG. 2. Rb^+ ion current *versus* time for various wire temperatures. Time is plotted to the left.

⁷ W. E. Forsythe and A. G. Worthing, *Astrophys. J.* **61**, 146 (1925).

⁸ J. Zemel, dissertation, Syracuse University (unpublished).

by the expression

$$I_+ = \frac{d}{dt} \left[e^{-t/\tau_i} \int_0^t f(t') e^{t'/\tau_i} dt' \right], \quad (1)$$

and the mean lifetime will be

$$\tau_i = \left[(d/dt) \ln I_+ + (1/I_+) (df/dt) \right]^{-1}. \quad (2)$$

For data taken for times after $\dot{f}(t)=0$, the second term on the right in Eq. (2) could be neglected and there was no need to know the exact shape of the chopped pulse shape. A value for τ_i at each temperature was taken from a plot of $\ln I_+$ versus time. Figure 3 shows a set of values of τ_i as a function of $1/T$ for a clean, etched W crystal. The inset shows the $\ln I_+$ —time plot for the temperature marked by the arrow.

It was found that the data could be represented by the equation

$$\tau_i = \tau_i^0 \exp(Q_i/kT).$$

The significance of the parameters Q_i and τ_i^0 will be discussed in the next section.

The slope of the $\ln \tau_i$ versus $1/T$ curves, Q_i was reproducible to within ± 0.05 ev. With the known accuracy in temperature ($\pm 5^\circ\text{K}$) and time ($\pm 2\%$), the absolute accuracy of the measurement is expected to be also about ± 0.05 ev.

IV. THEORETICAL BACKGROUND

It was obvious from the behavior of τ_i with temperature that a reaction rate of some kind had been measured. Since a number of different processes are known to take place, it was not equally obvious that the measured rate was that resulting from passage across a desorption barrier. The following events are assumed to occur:

(a) Adsorption from the beam: The evidence obtained by Taylor,³ for Cs on W, seems to indicate that the adsorption is not activated, i.e., the adsorption rate is not temperature dependent.

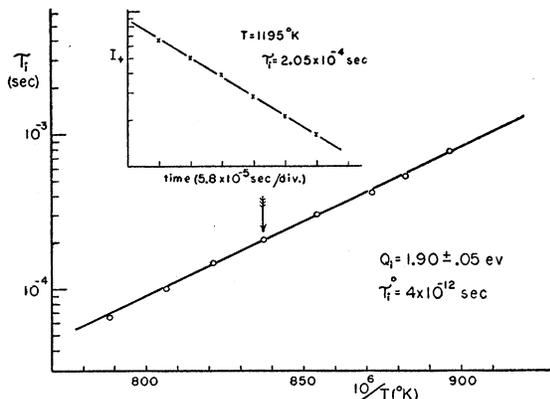


FIG. 3. Rb⁺ mean desorption lifetime versus $1/T$ for an "essentially clean" etched W crystal.

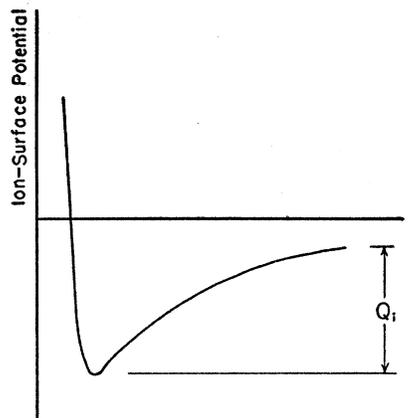


FIG. 4. Assumed potential for the Rb⁺ surface interaction as a function of ion-surface separation, r .

(b) Ionization of the Rb: Very few data exist concerning the rate of ionization. It is expected to be of the order of electronic transitions, i.e., 10^{15} /sec. We have data⁹ which show that the mean adsorption lifetime of the Rb which evaporates as neutral atoms, is different from τ_i . This indicates that atoms and ions exist on the surface in two discrete states and thus the ionization must take place rapidly compared to the lifetime on the surface.

(c) Surface migration after adsorption and before desorption: Previous measurements¹⁰ indicate that the migration activation energy for alkali metals on tungsten is of the order of 1 ev, or about half that which we have observed from the $\ln I_+$ — $(1/T)$ plots.

It seems certain, therefore, that the desorption rate was determined by a surface barrier. Another point, which should be mentioned, is the effect of Rb-Rb interactions when the surface concentration becomes high. Becker¹¹ has found that the interaction is negligible for Cs concentrations on W below about 10^{12} atoms/cm². In the present experiments, the desorption rate remained constant when the surface coverage was varied from 10^9 to 10^{10} atoms/cm².

The adsorption process may be represented by a group of non-interacting particles trapped behind a potential barrier of the form shown in Fig. 4. All that can safely be assumed is that for large r , the potential should be a classical image potential. The particles are assumed to be in quasi-equilibrium with the tungsten lattice at temperature T . The particles are assumed to escape from the potential well at such a low rate that the methods of the so-called irreversible thermodynamics can be applied. Calculation of escape rate for such a system has been made in several ways.^{12,13} For the present purpose, however, we have chosen the "transi-

⁹ F. L. Hughes, following paper [Phys. Rev. **113**, 1036 (1959)].

¹⁰ J. A. Becker, Trans. Faraday Soc. **32**, 1402 (1936).

¹¹ J. A. Becker, N. Y. Acad. Sci. **58**, 723 (1954).

¹² H. A. Kramers, Physica **7**, 284 (1940).

¹³ S. Chandrasekhar, Revs. Modern Phys. **15**, 65 (1943).

tion state" approximation, because it appears to give some physical insight into the significance of the parameter τ_i^0 . The rate will be given by¹⁴

$$P_i = 1/\tau_i = (kTF'/hF) \exp(-Q_i/kT);$$

$$\tau_i^0 = hF/kTF', \quad (3)$$

where Q_i is the barrier height, F and F' are, respectively, the statistical mechanical partition functions for the ion in the adsorbed state and in the transition state, and k , h , and T have their usual significance.

According to the theory, Eq. (3) should be valid, provided that the particles in the adsorbed state are in equilibrium with the particles in the transition state. For this problem, at least, the transition state is ill-defined and no calculations for F' can be made. This may be a reflection of the fact that the "transition state" is not a physical observable state in the usual sense of the word.

The equilibrium requirement may be restated in two equivalent ways. The theory should be valid if, in the process to be described, (a) the value of τ_i is long compared to the lattice-ion collision time (which is approximately equal to τ_i^0), or (b) the relationship $Q_i > 20kT$ is approximately true. Thus Eq. (3) should apply to the ion desorption case. There is another requirement which may be stated (in Chandrasekhar's theory, the "dynamical friction" is required to be small) in terms of information theory: the rate of change of population in the adsorbed state must not be greater than the rate at which information about the change is propagated to the exterior of the potential well.

In the past, a number of authors^{15,16} have assumed that $(\tau_i^0)^{-1}$ should be a constant of the order of the highest lattice vibration frequency of the adsorbing surface, that is, about 10^{13} /sec. To see that this is not exactly the case, one need only consider a one-dimensional, semi-infinite lattice of atoms with an atom of different species bound to one end of the chain. It is obvious that the finite termination of the lattice will modify the classical vibrations which the lattice imparts to the adsorbed atom and equally obvious that the adsorbed atom's behavior will depend strongly upon the way in which the atom is bound. An additional perturbation would occur if a contamination atom were inserted between the lattice and the adsorbed atom.

Some insight into the physical significance of τ_i^0 may be obtained by a crude calculation of the partition function F . Assuming a harmonic potential for adsorbed ion movement normal to the surface, and assuming almost free, two-dimensional, gas statistics for motion parallel to the surface, then

$$\tau_i^0 \propto [1 - \exp(-h\omega_0/kT)]^{-1} (2\pi m^* kT/h^2), \quad (4)$$

¹⁴ Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 354.

¹⁵ J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, Oxford, 1946).

¹⁶ J. H. DeBoer, *The Dynamical Character of Adsorption* (Oxford University Press, Oxford, 1953).

where ω_0 is the zero-point vibrational frequency and m^* is the effective mass of the particle in surface migration.

For the high-temperature region, the harmonic oscillator contribution is approximately $(\omega_0)^{-1}$ which, to some extent, is justification for Frenkel's argument. The value of m^* will depend on the periodic lattice potential over which the migration occurs and should be affected by lattice disorder or by impurities imbedded in the surface.

From these considerations it seems reasonable to interpret variations in τ_i^0 as due primarily to changes in adsorbate environment very near the surface, and in particular, to changes which affect the shape of the potential well near its minimum.

IV. EXPERIMENTAL (PART B)

1. Tungsten Surface Preparation

For surface measurements, it is desirable to have as uniform a surface as possible. This implies a well-defined, ideal crystallographic plane of a single crystal. Although surface properties are expected to be qualitatively the same for two different crystallographic planes of the same substance, measurements made on a surface containing a distribution of different planes may give results which will not resemble those for any one of the planes. The reason for this is that the ion/atom ratio,¹⁷ evaporation probability, surface mobility (for high alkali concentrations), and electron work function are dependent on the crystallographic plane. A macroscopic surface, with several planes exposed, will have surface ionization properties in which all the above parameters enter in an exceedingly complicated non-linear "average."

Since previous surface work has shown such phenomena as straight-line Richardson plots for thermionic emission, etc., it appears that the investigations were made upon surfaces which had inadvertently been made uniform or nearly so. Taylor's³ method of "aging" tungsten, to produce a stable surface, apparently also produced a homogeneous surface. His data, showing the behavior of the Cs-W ionization fraction during the "aging" process (reference 3, p. 431), are very illuminating.

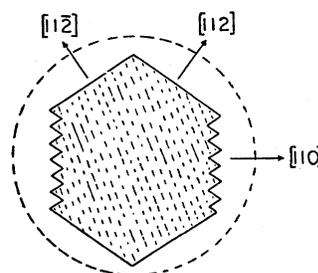


FIG. 5. Schematic of the etched W cross section; $(1\bar{1}0)$ plane parallel to paper. The arrows indicate directions for which thermionic work function data were taken. The dotted circle indicates approximately the original cross section.

¹⁷ This term is found from the Langmuir-Saha equation [see J. Zemel, *J. Chem. Phys.* 28, 410 (1958)].

For the purposes of this work, an attempt was made to produce a macroscopic surface which would have the properties of a single crystallographic plane of tungsten. This was accomplished by etching a tungsten single-crystal wire.^{18,19}

Figure 5 shows a schematic view of the crystal cross section after etching. The plane of the paper is the $(\bar{1}\bar{1}0)$ plane of the crystal. The surface consists of four large fairly smooth surfaces, which are normal to the (112) directions, and a series of smaller surfaces which are arranged in "steps" along a plane which is normal to the $[110]$ directions. Although it was not possible to make crystallographic goniometer measurements, it is believed that the faces of the steps are crystallographically the same as those of the four large surfaces. A series of parallel "grooves" were found on both the "step" faces and on the large faces normal to the $[112]$ directions. The "grooves" are at an angle of about 60° with respect

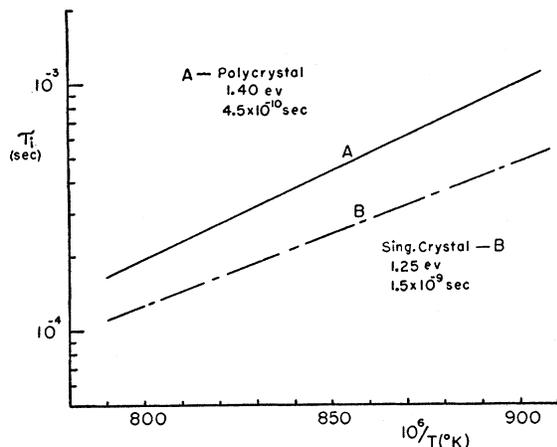


FIG. 6. Rb^+ lifetime data for a polycrystalline wire and for the etched crystal; contamination was about $1.0\theta_1$.

to the wire axis and are about 1μ apart and 1μ deep (these are shown in micrographs, reference 18). Thus it appeared that, on a macroscopic level, the surface was made up of many crystallographically equivalent (112) planes. The presence of the "grooves," however, indicate that these are not "ideal" (112) planes on a microscopic level. Work function measurements¹⁸ indicate that the surface has a superstructure of (112) planes with a uniform microstructure of (110) planes.

Thermionic work function measurements were made with an apparatus like that of Nichols.²⁰ Emission in the $[110]$, $[112]$, and $[112]$ directions was the same,

¹⁸ Hughes, Levinstein, and Kaplan, preceding paper [Phys. Rev. **113**, 1023 (1959)].

¹⁹ Obtained from Kulite Tungsten Company, Union City, New Jersey. The list of impurities given by the manufacturer shows the usual manufacturing fluxes. It has been found that single crystals made from this wire contain about 1/100th of the alkali impurity contained in crystals made from the "G.E. 218" wire and that there is no spectroscopically observable carbon content.

²⁰ M. H. Nichols, Phys. Rev. **57**, 297 (1940).

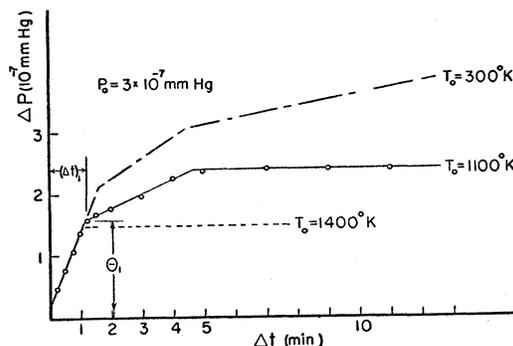


FIG. 7. Flash filament data; ΔP is proportional to the amount of residual gas contamination accumulated in Δt seconds after cleaning. The temperature, T_0 , is the wire temperature during the interval of contamination deposit. See text for explanation of θ_1 and $(\Delta t)_1$.

$\phi_0^* = 5.25 \pm 0.05$ v. The value was confirmed by Na surface ionization fraction measurements with a Na beam which simultaneously covered the surfaces normal to the $[110]$ and $[112]$ directions indicated by Fig. 5.

Figure 6 shows the Rb^+ lifetime for a polycrystalline²¹ and an etched single-crystal tungsten wire under comparable contamination conditions. The data for contaminated wires are shown since the polycrystalline surface could not be completely cleaned by high-temperature heating without changing the crystal structure. It was estimated from etched-wire contamination results, that the "clean" value of Q_i for the polycrystalline surface would be about 2.15 eV as compared to the "clean" value for the etched crystal of 1.90 eV (see Fig. 3).

2. Residual Gas Contamination Effects

Contamination measurements were made by use of the "flash filament" technique.²² The wire was cleaned by a 2300°K "flash" for one second and cooled to a lower temperature T_0 . After a time interval, Δt , the wire was again flashed. The residual gas which had been adsorbed during the interval was desorbed by the flash and caused a rise ΔP , in the system pressure. If the area, A , of the wire and the system volume, V , are known, then the contamination concentration, after time Δt , is given by²² $\theta = 8.7 \times 10^{19} (V/A) (\Delta P) / \text{cm}^2$.

Figure 7 shows the results. Although $T_0 = 1100^\circ\text{K}$ was chosen as the standard reference temperature, the dotted curves show approximately the behavior at $T_0 = 300^\circ\text{K}$ and 1400°K . Even though the system pressure remained constant over several days the time, $(\Delta t)_1$, required to produce a contamination θ_1 (see Fig. 7), increased from an initial value of 30 seconds to 3

²¹ No irreversible changes were observed in the raw wire until it had been heated above 1800°K .

²² J. A. Becker and C. H. Hartman, J. Phys. Chem. **57**, 157 (1953). Recent evidence, to be discussed later, indicates that the technique, as used here, is not suitable for work with oxygen. However, it is expected that the results are qualitatively correct and reproducible enough so that mean Rb^+ lifetimes may be measured with "relative" contamination as a parameter.

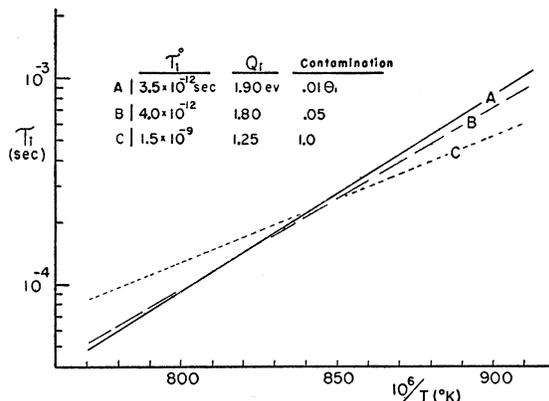


FIG. 8. Rb⁺ lifetime data for the etched W crystal for various contamination concentrations. θ_1 is of the order of 10^{13} atoms/cm². (See text.)

minutes. This indicated that the contamination constituent of the residual gas (perhaps O₂, CO, or CO₂) was being removed by the gettering action of the oven chamber.

Since the vacuum system (Fig. 1) had a large pump manifold, the volume V could not be precisely determined. Therefore an auxiliary mercury-pumped vacuum system resembling that of Becker²² was constructed. With this system it was possible to make measurements like those shown in Fig. 7 for oxygen-containing gases ranging from pure oxygen, and dry air, to the equilibrium residual gas. It was found that for $T_0 = 1100^\circ\text{K}$, there was comparatively little variation in θ_1 ($0.8 \times 10^{13} < \theta_1 < 1.1 \times 10^{13}$ atoms/cm²) although the corresponding value of $(\Delta t)_1$ was shorter for the greater oxygen partial pressures. The work indicated that the contaminating gas is, or contains, oxygen. The equilibrium residual gas in the auxiliary system, after bake-out and degassing, still contained a much greater partial pressure of contaminating gas than the gettered main system (Fig. 1). The contamination rate was found to be the same for the auxiliary system at 5×10^{-9} mm Hg, and the gettered system at 5×10^{-7} mm Hg.

The desorption experiments of Hagstrum²³ and Ehrlich²⁴ were duplicated crudely. The wire was cleaned, allowed to adsorb contamination a few minutes, and cleaned by increasing the temperature very slowly. The desorbed gas came off in three distinct bursts at approximately 500°K , 1150°K , and 1750°K , indicating three different adsorption states. The desorption thus fits the pattern observed by Becker and Brandes²⁵ for oxygen desorbed from a plane of a field emission point.²⁶

²³ H. D. Hagstrum, Rev. Sci. Instr. **24**, 1122 (1953).

²⁴ G. Ehrlich, J. Chem. Phys. **23**, 1543 (1955).

²⁵ J. A. Becker and R. G. Brandes, J. Chem. Phys. **23**, 1323 (1955).

²⁶ Until fairly recently, "chemical" adsorption was visualized as occurring in "layers" each layer consisting of about 10^{14} atoms/cm². Now, however, it seems more reasonable to view the process as a filling of adsorption "traps," each kind of "trap" having a different binding energy. In particular G. Ehrlich [J.

For low partial pressures of oxygen, the desorbed gas peaks occurred at the three previously mentioned temperatures and in addition there was a peak, at about 1000°K , representing an unknown gas. For most conditions observed, the unknown gas was less than 10% of the total quantity of adsorbed gas.

As mentioned above,²² the flash filament technique, at least in its present form, is not suitable for quantitative work with reactive gases. Hickmott²⁷ and Becker²⁸ have found that the ionization gauge effects the measurements and that some desorbed oxygen passes off as WO₂ when the wire is flashed. For present purposes, however, a relative-contamination parameter was valid and was taken to be the fraction of θ_1 atoms/cm². That is, if the Rb⁺ mean lifetime data were taken after x seconds of contamination deposit, under conditions which build up a contamination θ_1 in $(\Delta t)_1$ seconds ($T_0 = 1100^\circ\text{K}$), then the lifetime data were labelled with the parameter $[x/(\Delta t)_1]\theta_1$. The true contamination level is expected to be at least twice²⁹ that indicated by assuming the measured value of $\theta_1 \approx 1 \times 10^{13}$ atoms/cm².

Figure 8 shows the effect of contamination on the Rb⁺ lifetime on etched tungsten. It should be noted that a drastic change in adsorption energy occurred with fairly moderate changes in the mean life. At least for this system, the reaction rate is not totally specified by the activation energy.

A number of miscellaneous effects have been observed which have a bearing on contamination effects. Since there are very few data available, these effects will merely be listed.

(1) Carbon contamination of less than one part in 10^6 (produced by heating the tungsten for 10 minutes at 2600°K in a system with oil diffusion pumps) lowered the value of τ_i^0 by a factor of three but did not change Q_i from the uncontaminated value. Becker³⁰ has observed carbon on field emission points. Apparently, at low concentrations, the carbon atoms remain below the surface for most of the time. Occasionally an atom will rise to the surface, remain for a while, and diffuse back into the surface. Thus, this form of contamination would, on the average, be expected to affect the form of the Rb⁺ binding energy only at small distances from the surface.

(2) No significant differences have been observed in τ_i for Rb⁺ obtained from Rb metal, RbCl, and RbI.

Chem. Phys. **24**, 482 (1956)] has found that even in the early stages of adsorption after cleaning, several of the different "traps"²⁷ may contain nonequilibrium concentrations of atoms and that some, if not all, of the atoms are mobile.

²⁷ T. W. Hickmott and G. Ehrlich, J. Chem. Phys. **24**, 1263 (1956).

²⁸ J. A. Becker, Third Field Emission Symposium, Pennsylvania State University, June 27, 1957 (unpublished).

²⁹ Independently, J. A. Becker has observed desorption structure such as that of Fig. 7 (reference 28). By measuring desorption by pressure decrease in a controlled-flow dynamic system, he has obtained data without WO₂ formation. He estimates (private communication) that about 50% of the adsorbed material is lost during flashing (presumably as WO₂).

³⁰ J. A. Becker (private communication).

Furthermore, no differences were observed after flushing the system with Cl_2 gas (producing an estimated Cl_2 partial pressure of 1×10^{-7} mm of Hg).

V. DISCUSSION

The reasons for desiring a uniform surface require no emphasis. Until further work is done with etched W surfaces, however, it cannot be absolutely certain that etching produces the uniformity indicated by the above-mentioned work function, surface ionization, and oxygen desorption data. It would be very desirable to obtain velocity distribution measurements of thermionic electrons under conditions such as those obtained by Shelton.³¹

In the specification of surface cleanliness, the phrase, "atomically clean" is sometimes used. This implies that, even on an atomic scale, there are no foreign adsorbed atoms. This condition can only be realized for tungsten above 2000°K , and for a field-ion microscope³² point under certain operating conditions. A more practical definition of a clean surface is given by the term "essentially clean"²⁸; that is, the surface is so clean that any further decrease in contamination will not affect the surface parameter which is being measured.

Figure 9 shows a curve for the desorption energy at various levels of residual gas contamination. The concave-down slope of the curve in Fig. 9 agrees with crude theoretical calculations for low contaminations. It is expected that any decrease in contamination will change the value of Q_i by a quantity that is less than the experimental error of ± 0.05 eV; thus data taken at the smallest value of contamination may be classed as "essentially clean." These data were taken within five seconds after cleansing the wire in a gettered system. The gas contamination rate corresponded to that measured in the equilibrium residual gas of an ungettered, mercury-pumped system at 5×10^{-9} mm Hg. At extremely high contamination values (greater than $2\theta_1$) the experimental slope increases and Q_i becomes greater than the clean value.

As mentioned previously, the flash filament data can have, at best, only qualitative value. However, in view of the rather unusual structure exhibited by the $\Delta P-\Delta t$ curves of Fig. 7, some discussion seems warranted. If the sticking probability, S , is defined as the ratio of atoms/cm² adsorbed to atoms/cm² striking the surface, then $\Delta P/\Delta t$ is proportional to S . It is tempting to associate the three values of S (at $T_0=300^\circ\text{K}$) with the three desorption energies. With this line of reasoning, one could assume that the initial value of S would persist until the lowest desorption state was filled. Then the second value of S would correspond to the filling of

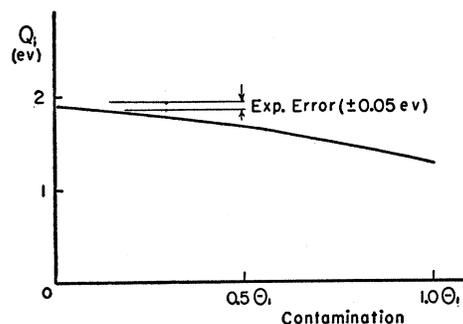


FIG. 9. Rb^+ desorption energy Q_i , for various contamination concentrations.

the next lowest state, and so on. This simple picture, however, is complicated by two facts: (1) The adsorbed particles are likely to be mobile above 1000°K ,²⁵ and (2) in the present work, it has been found that (at $T_0=300^\circ\text{K}$) all three adsorption states attain some population while the initial value of S still prevails. A satisfactory theory must be complex enough to fit these additional facts.

VI. SUMMARY

The mean adsorption lifetime has been measured for Rb^+ ions adsorbed on "essentially clean," etched tungsten single crystals. No Rb-Rb interaction was observed at the Rb surface concentrations used.

Adsorption lifetime parameters, τ_i^0 and Q_i , were found to be strongly dependent on surface crystal structure. All observations indicate that the etched surface is extremely uniform, with properties that approximate those of a crystallographically pure plane of tungsten.

Contamination measurements indicate that the best data are "essentially clean." The measurements suggest that the residual gases in conventional ungettered vacuum systems contain a great deal of strongly adsorbing gas and that data taken with such a system at 5×10^{-9} mm of Hg may be slightly contaminated within a few seconds after surface cleaning. Assuming conservatively that the experimental value of θ_1 (1×10^{-13} atoms/cm²) is too low by a factor of ten, the best value of Q_i (Fig. 9) will be changed by 0.01 to 0.02 eV by a contamination concentration of 10^{12} atoms/cm²; that is, by contamination of one percent of a conventional "monolayer" (see reference 27).

VII. ACKNOWLEDGMENTS

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³¹ H. Shelton, Phys. Rev. **107**, 1553 (1957).

³² E. W. Muller, Z. Naturforsch. **11a**, 88 (1956).

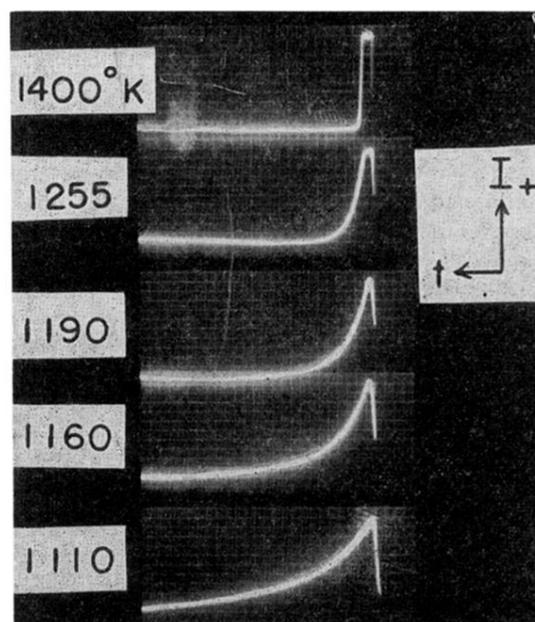


FIG. 2. Rb^+ ion current *versus* time for various wire temperatures.
Time is plotted to the left.