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THERMAL IONIZATION AT HOT METAL SURFACES

Joseph R. Werning

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THERMAL IONIZATION AT HOT METAL SURFACES

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September 1958

ABSTRACT

Ionization on hot tungsten, tantalum, and rhenium surfaces was studied. An atomic beam of neutral atoms effused from a Knudsen-type effusion vessel and struck a hot filament of the metal being studied. A temperature-dependent fraction of these atoms was ionized. This filament served as the ion source of a 60-degree-sector single-directional focusing mass spectrometer. According to the Saha-Langmuir theory of surface ionization the temperature dependence of ionization is related to the difference between the ionization potential of the impinging atom and the work function of the surface under consideration.

The temperature dependence of the positive ion current produced by barium atoms impinging onto tungsten, tantalum, and rhenium filaments was measured over a wide range of filament temperatures. At temperatures higher than 2500°K excellent agreement with the Saha-Langmuir theory was obtained. Using the value of 5.21 electron volts for the ionization potential of barium we obtain 4.58 ± 0.01 ev for the work function of tungsten and 4.23 ± 0.03 ev for the work function of tantalum. Both values are in excellent agreement with generally accepted values determined by independent means. On rhenium we find the Ba^+ ion current to be essentially independent of temperature, indicating a work function equal to or appreciably higher than the 5.21 ev ionization potential of barium.

Using the strontium ionization potential of 5.69 ev we obtain a tantalum work function of 4.17 ev, a value in reasonable agreement with that above. The strontium study yields a value of 5.17 ± 0.02 ev for the work function of rhenium, a value consistent with the study noted above.

The positive ion current produced by uranium atoms impinging onto a tungsten filament indicates an ionization potential of 6.25 ± 0.02 ev for the uranium atom. This value is based on the 4.58 ev work-function value for tungsten indicated above.

The neodymium ion current produced on a tungsten surface indicates an ionization potential of 5.10 ± 0.04 ev for neodymium. This is based on the 4.58 ev tungsten work function.

At temperatures below $2000^{\circ}K$ we found order-of-magnitude deviations from the extrapolated Saha-Langmuir theory. For barium and strontium the positive ion current was in excess of the value predicted by extrapolation of the high-temperature straight line. For uranium and neodymium the low-temperature currents were generally less than the extrapolated values. These effects cannot be explained in terms of an altered electronic work function caused by the adsorption of impurity atoms, such as oxygen, from the gas phase of the system. We find, instead, that positive ions are produced in chemical reactions taking place on the surface of the metal. Barium reacts readily with oxygen from the gas phase and with oxygen and fluorine diffusing from the interior of the metal. The products of these reactions decompose, yielding barium ions in high efficiency. BaF^+ ions are also observed. The behavior of strontium is similar to the behavior of barium. Uranium atoms react with oxygen on the surface, producing UO^+ and UO_2^+ ions, the uranium ion current being decreased by the presence of oxygen. The behavior of neodymium is similar to the behavior of uranium, with the exception that no NdO_2^+ ions are observed.

We find, in general, that at temperatures below $2000^{\circ}K$ each system has its own chemical properties, and that these must be resolved on an individual basis rather than by recourse to general surface properties such as bulk work functions, surface inhomogeneties, or reflection coefficients.

THERMAL IONIZATION AT HOT METAL SURFACES

INTRODUCTION

It has been generally believed for a number of years that ionization phenomena on hot metal surfaces are adequately described by the Saha-Langmuir theory of surface ionization. Experimental agreement with the theory has in general been qualitative rather than quantitative, and there are very few cases in which quantitative agreement has been obtained. These few cases have been limited to several of the alkali metals evaporating from tungsten surfaces. Here the efficiency of the process is so great that the true Saha-Langmuir type of ionization tends to swamp out any other mechanism that might tend to compete. In order to get reasonable agreement, various authors have used values for the tungsten work function which have varied by as much as 0.2 electron volts.

Deviations from the Saha-Langmuir theory have been attributed to the nonhomegeneity of the crystalline surface under consideration, to the effect of adsorbed fractional layers of oxygen on the bulk work function of the surface, to various reflection coefficients, and to the possibility that the Saha-Langmuir theory does not adequately account for the extra valence electrons encountered in cases other than the alkali metals.

In the present work we find essentially quantitative agreement with the Saha-Langmuir theory at high temperatures where other mechanisms do not interfere. This agreement includes barium ionizing on tungsten, tantalum, and rhenium, and strontium ionizing on tantalum and rhenium. Further, we have obtained reasonable evidence that the actinide element uranium and the lanthanide element neodymium ionize on tungsten according to theory, but in these cases there are no reliable independent measurements of the ionization potentials available.

In addition we find that most deviations from the Saha-Langmuir theory can be explained in terms of an entirely different mechanism, that of simple chemical reactions between the ionizing species being studied and the large quantities of impurities present even in "well aged" filaments of the high-temperature metals such as tungsten, tantalum, and rhenium. In addition, in many experiments the vacuum attained was not sufficient to reduce atmospheric sources of oxygen to below the interference level. The impurities of particular concern are fluorine and oxygen. We also have indications that alkali metal impurities, particularly potassium, interfere in certain cases, but we do not have quantitative evidence to verify this. Fluorine and oxygen can, and sometimes do, account for order-of-magnitude discrepancies in both the ionization efficiency and the temperature dependence of the ionization efficiency.

Essentially, our experiments indicate that the Saha-Langmuir theory describes only one of several mechanisms responsible for surface ionization. While apparently correct in principle, even the purest available metals contain impurities which can completely mask the Saha-Langmuir process, particularly when the efficiency by this process is low.

THEORETICAL BACKGROUND

Much of this work has been concerned with testing the validity of the Saha-Langmuir theory of surface ionization. This theory was derived by Langmuir[1] and has as its basis the work of Saha, which relates the concentrations of ions, atoms, and electrons in a gas in thermodynamic equilibrium.[2] The Saha equation may be written in the following form:

$$\frac{n_+ n_-}{n_a} = \left(\frac{2\pi m_e k T}{h^2}\right)^{3/2} \left(\frac{\omega_+ \omega_-}{\omega_a}\right)_e^{\frac{-I}{kT}}, \qquad (1)$$

where n = number of particles,

ω = statistical weight of particles,

m_e = electron rest mass,

I = ionization potential of the atom,

k = Boltzman constant,

h = Planck constant,

T = temperature (degrees Kelvin),

and $+$, $-$, a represent positive ions, electrons, and atoms.

According to kinetic theory the number of particles striking one surface of a unit cube in unit time is related to the number of particles in the cube by[3]

$$N_t = n_o \sqrt{\frac{k\,T}{2\,\pi\,m}}\,, \tag{2}$$

where N_t = number striking wall per unit time,

n_o = number of particles in cube.

The number getting through the surface is this number minus the number reflected:

$$N = N_t\ (1 - r). \tag{3}$$

Multiplying by unit charge, we have

$$i = N\epsilon = N_t\ \epsilon\ (1 - r), \tag{4}$$

where i = "current" of particles,

ϵ = unit charge of electron.

Sommerfield's modified Richardson Equation may be written[4]

$$i_- = (1 - r_-)\ 2\pi\, m_e\, \epsilon\, k^2\, T^2\, \omega_-\, h^{-3}\, e^{-\frac{\phi_-}{kT}}\,, \tag{5}$$

where ϕ_- = electron work function of the surface.

By combining Eqs. (4) and (5), putting in the values of N_t from Eq. (2), and substituting the resulting values of n into Eq. (1), we obtain

$$\frac{i_+}{i_a} = \frac{\omega_+}{\omega_a}\left(\frac{1 - r_+}{1 - r_a}\right) e^{(\phi_- - I)/k\,T}\,, \tag{6}$$

which is generally known as the Saha-Langmuir equation. This relationship assumes that the system is in thermodynamic equilibrium, a condition which we verify primarily by the agreement of our results with theory.

For $I \gg \phi_-$, $i_+ \ll i_a$, i_a is approximately constant, and it is valid to write

$$\ln i_+ = \ln i_a\ \left(\frac{\omega_+}{\omega_a}\right)\left(\frac{1 - r_+}{1 - r_a}\right) + \frac{\phi_- - I}{k\,T}\,, \tag{7}$$

and if no temperature-dependent reflections occur this reduces to

$$\ln i_+ = \text{constant} + \frac{\emptyset_- - I}{k\,T} \quad . \qquad (8)$$

On plotting $\ln i_+$ vs $1/kT$ one should obtain a straight line with a slope equaling $\emptyset_- - I$. A test of the Saha-Langmuir relationship is then to measure the temperature dependence of the positive ion current of an atom of known ionization potential from a surface of known work function.

If $I = \emptyset_-$, the exponential term disappears and the ionization efficiency becomes temperature independent. A plot of $\ln i_+$ vs $1/kT$ should yield a straight line with zero slope.

When $I \ll \emptyset_-$, the ionization is essentially 100% complete and again one should obtain a straight line with zero slope.

In all other cases the data must be treated by plotting $\ln i_+/i_a$ vs $1/kT$.

EXPERIMENTAL BACKGROUND

The work of Langmuir,[1] Ives,[5] Meyer,[6] and Becker[7] on the surface ionization of cesium on tungsten and tungsten oxide forms the classical background for this study. The result of these works was the qualitative verification of the Saha-Langmuir equation for the ionization of cesium on tungsten surfaces partially covered with adsorbed layers of cesium atoms. Killian carried out similar measurements on potassium and again obtained results which were in qualitative accord with theory.[8] These investigators employed a technique that has become known as the bulb method. The method consists essentially of sealing a tungsten wire and a concentric cylindrical collector into a bulb containing vapors of the alkali metal being studied. The rate of arrival of the alkali metal at the surface of the tungsten wire is then controlled by regulating the temperature of the bulb in which the system is contained. At various arrival rates at the tungsten surface the temperature of the tungsten wire is varied and the positive ion current arriving at the collector plate is recorded. However, at tungsten wire temperatures higher than about 1500°K, photoelectrons are emitted from the collector and add to the recorded positive ion current.

This phenomenon prevented these workers from extending their data to temperatures high enough that cesium and potassium would have been striking a clean tungsten surface and evaporating essentially instantaneously as either ions or atoms in a ratio presumably predicted by the Saha-Langmuir theory.

The first attempt to overcome this difficulty was made by Morgulis.[9] Using the magnetron cutoff principle to prevent photoelectrons from striking the hot tungsten wire, he was able to obtain measurements of the positive ion currents up to about 2200°K without obtained interference from the electrons. His measurements for the ionization efficiency of sodium on tungsten agreed with the Saha-Langmuir theory to within an order of magnitude.

An atomic beam impinging on a hot metal surface was first utilized by Coply and Phipps.[10] By drastically reducing the level of alkali metals in the system and by arranging the collecting cylinder so that it could be thoroughly heated and outgassed, they were able to reduce the photoelectron current to a negligible value at 2400°K, and by running the freshly outgassed system at higher temperatures they were able to obtain some data as high as 3000°K with essentially no photoelectron interference. (It is apparent that the photoelectrons resulted from the lowering of the photoelectric threshold owing to the adsorption of alkali metals on the collector plate.) By this technique they were able to obtain results that are in essentially quantitative agreement with the Saha-Langmuir theory. Although their data depart somewhat from theory at both high and low temperature, they were able, over a wide temperature range, to obtain a plot which gave a tungsten work function of about 4.51 ev. This is one of the few values in the literature that is in agreement with the electronic work function as determined by the standard electron-emission technique.

Hendricks, Phipps, and Copley have studied the ionization of the potassium halides on tungsten.[11] At low temperatures they obtained appreciably more ionization than predicted by the Saha-Langmuir theory. This they attributed to the formation of a partial film of halide which is stable at relatively high temperatures, and has local work functions high enough to effect essentially 100% ionization of the alkali atoms contacting these spots. It should be noted that in these experiments with the alkali halides it is assumed that the halide decomposes to form the alkali metal and the halogen, and that these two species then evaporate and ionize according to the Saha-Langmuir theory. Datz and Taylor have done similar work with the potassium halide and reported essential agreement with the Saha-Langmuir theory when the metal being bombarded was tungsten, but for platinum and platinum-tungsten alloys they were unable to obtain agreement with theory.[12] They attribute this discrepancy between experiment and theory to reflections of the impinging halide molecule, which amount to approximately 99% of the impinging beam.

Johnson and Phipps[13] and Ionov[14] have worked with the sodium halides. Their work is in essential agreement and they report a high-temperature excitation energy of 0.2 ev, as contrasted with a theoretical value of 0.6 ev for ionization on tungsten.

In a brief note Guthrie reports work on the barium-tungsten system, noting that at high temperatures no temperature dependence of the barium ion current is observed.[15] This was probably due to the lack of sensitivity of his measuring device. Morosov has also measured the ionization of barium on tungsten.[16] In addition to unexpectedly high efficiency at low temperatures he obtains a high-temperature activation energy of 0.39 ± 0.06 ev, as compared with a theoretical value of 0.63 ± 0.06 ev. He attributes the low-temperature increase in efficiency to the change in work function of the surface due to adsorbed oxygen. In explaining the high-temperature slope he considers the Darwin-Fowler modification of the Saha-Langmuir theory, which accounts for the excited states of the barium ions and atoms. Up to 2500°K the theoretical slope is not changed by this modified form, and at higher temperatures the correction is so slight that Morosov considers it to be only a very slight improvement in agreement. He suggests that the deviation of experiment from theory may be explained by the fact that the Saha-Langmuir equation does not make allowance for barium's having two valence electrons instead of one.

Datz and Taylor have studied the ionization of all the alkali metals on tungsten, tungsten-platinum alloys, and platinum.[17] For tungsten they claim agreement with the Saha-Langmuir theory, using work-function values for tungsten that are not unreasonable when compared with the best data for electronic work function. For the alloy and platinum the data are at wide variance with theory. As with the potassium halides, they attribute this discrepancy to some particularly reflective property of the platinum surface.

Romanov has investigated the ionization of lithium on tungsten, and notes some increase in efficiency above the predicted value at relatively low temperatures.[18] At high temperatures he obtains an activation slope of 0.6 to 0.7 ev, in contrast to the 0.85 ev value predicted by theory. He makes calculations which indicate that these discrepancies cannot be due to a change in work function of the surface caused by adsorbed oxygen. In addition he postulates and shows by calculations that the discrepancies can be accounted for by considering the inhomogeneity of distribution of the exposed crystalline planes of the surface. In this manner he postulates that the relatively high work-function planes of the tungsten lattice contribute a much larger fraction of the positive ions than one would expect. The theoretical aspects of this treatment have been worked out in detail by Zemel.[19]

Romanov and Starodubtsev have investigated the ionization of sodium on tungsten.[20] The results of their work are essentially in accord with the lithium work, that is, the slope of the high-temperature excitation line is somewhat too low and the low-temperature ionization efficiency is too high.

EXPERIMENTAL APPARATUS

A thermally generated atomic beam of the sample element was directed onto a hot tungsten, tantalum, or rhenium filament. This filament served as the positive ion source for a 60-degree sector, single-directional focusing mass spectrometer of 20-cm radius. The mass-separated positive ions were detected by means of an electron multiplier, integrated by a vibrating-reed electrometer and recorded on a Leeds and Northrup recording potentiometer. At all times the atomic beam intensities were kept low enough to prevent any appreciable fraction of one monolayer from being formed by adsorption. Typical ion currents were from 10^{-14} to 10^{-17} ampere.

The atomic-beam and ion-source assemblies, together with the necessary circuits, are shown in Fig. 1. A tantalum or tungsten Knudsen-type vessel A was heated internally by radiation or electron bombardment from a 0.010-in.-diameter tungsten wire, B. This vessel was supported by six small, sharply pointed tungsten or tantalum screws. Electrons and positive ions were separated from the atomic beam by properly biased grids, C. The entire region was surrounded by a tantalum heat shield. Stray electrons were further shielded from the ionization region by tantalum strips, D. The atomic beam effused from the crucible and passed down a 1/8-by-1/8-in. channel in the filament plate, E, and was collimated at F before striking the hot filament at G. The hot filament was a 0.001-by-0.030-in. ribbon of tungsten, tantalum, or rhenium. The magnetically operated shutter was at H. The positive ions were drawn into the region between Plate E and the drawing-out plate, slightly less positive with respect to ground than the 5000-volt potential on Plate E. Acceleration to ground was accomplished between Plates I and J. Focusing was assisted by the split plate K, one half of which was grounded and the other half used to apply a deflecting potential. Ions passed directly through the slit in Plate L into the tube of the mass spectrometer. All plates were separated and supported by threaded pyrex rods and pyrex spacers.[21] Plates were fabricated from nonmagnetic stainless steel sheet.

The magnetically actuated shutter devised to instantaneously interrupt the atomic beam was operated by a soft iron core placed in two concentric but axially displaced solenoids. The shutter mechanism operated inside of the vacuum chamber and was constructed of glass and clean metals to avoid the introduction of unknown impurities.

All gaskets in the entire vacuum system were copper or indium, and all valves were sealed with molten indium. Every precaution was taken to keep the system free of organic matter. Two mercury diffusion pumps were used in parallel and all traps filled automatically with liquid nitrogen. In the tight system the base pressure of noncondensables at liquid nitrogen temperature was about 5×10^{-9} millimeter of mercury. Runs were started after the source had been thoroughly out-gassed near operating temperatures and after the pressure in the source region had dropped below 1×10^{-7} mm Hg.

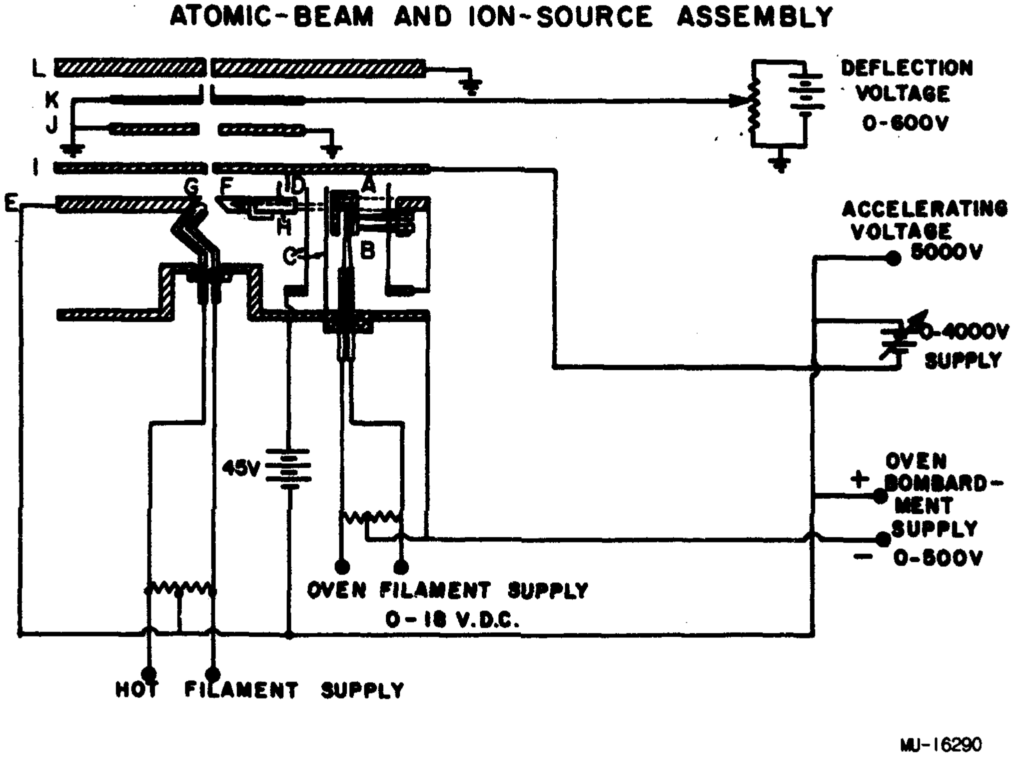

Fig. 1. Atomic-beam and ion-source assembly.

A 16-stage Allen-type electron multiplier with a maximum gain of about 10^9 was used at a gain of about 4×10^6 to detect the ion current. Integration was followed by measurement with a vibrating reed electrometer. Sensitivity was such that a single ion could be detected. Sharp peak resolution was obtained with the background usually amounting to a few ions per minute.

Temperatures were measured with a "Pyro-Optical Pyrometer" manufactured by The Pyrometer Instrument Company. The necessary corrections for emissivity of the filament and for transmission through the quartz window were applied. The tungsten emissivity data of Roeser and Wensel,[22] the tantalum data of Malter and Langmuir,[23] and the rhenium data of Sims, Craighead and Haffee[24] were used.

The assembled atomic-beam section is shown in Fig. 2. The top of the effusion cell is in the center. The tantalum support screws and deflection grids are visible. The atomic-beam and hot-filament assemblies are shown separately in Fig. 3, and connected -- ready for insertion into the mass spectrometer -- in Fig 4. The magnetically operated shutter assembly is not shown in these figures.

THE IONIZATION OF BARIUM ON TANTALUM

The high-temperature surface ionization of barium atoms impinging on a clean, well-aged tantalum surface follows the Saha-Langmuir equation. Analysis of the barium data yields a value of 0.98 ± 0.03 ev for the activation term in the Saha-Langmuir equation. Using the 5.21 ev ionization potential for barium reported by Moore,[25] this value yields a gross work-function for tantalum of 4.23 ± 0.03 ev, in reasonable agreement with the 4.19 ev value reported by Fisk[26] and also with our own determination by electron-emission measurements.

At lower temperatures competing chemical reactions cause a marked departure from the ionization efficiency predicted by the Saha-Langmuir equation. Of primary concern is the enhancement of the ionization efficiency by surface reactions with oxygen and fluorine. This increase in efficiency is attributable to the breaking of chemical bonds, hence the

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Fig. 2. Atomic-beam subassembly.

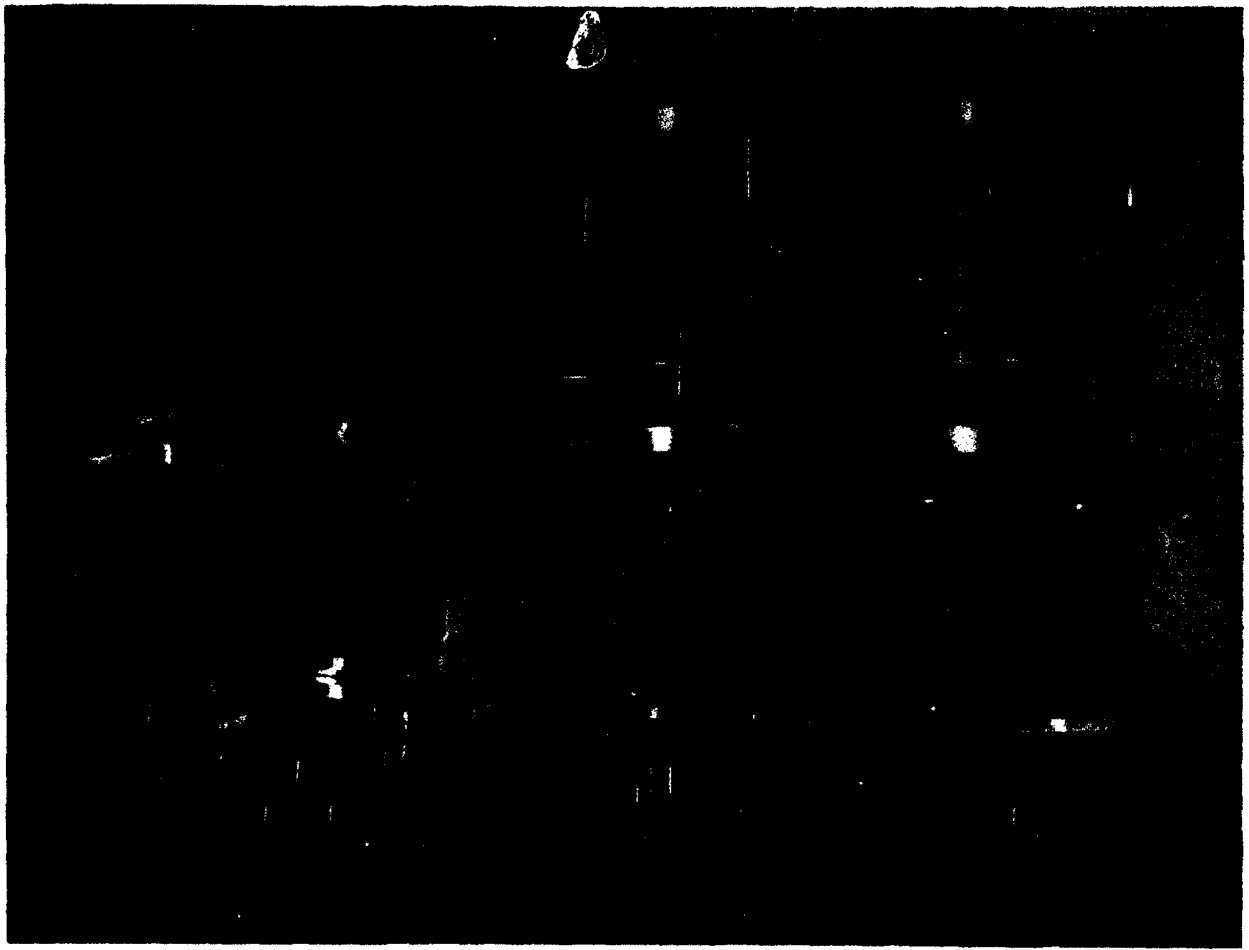

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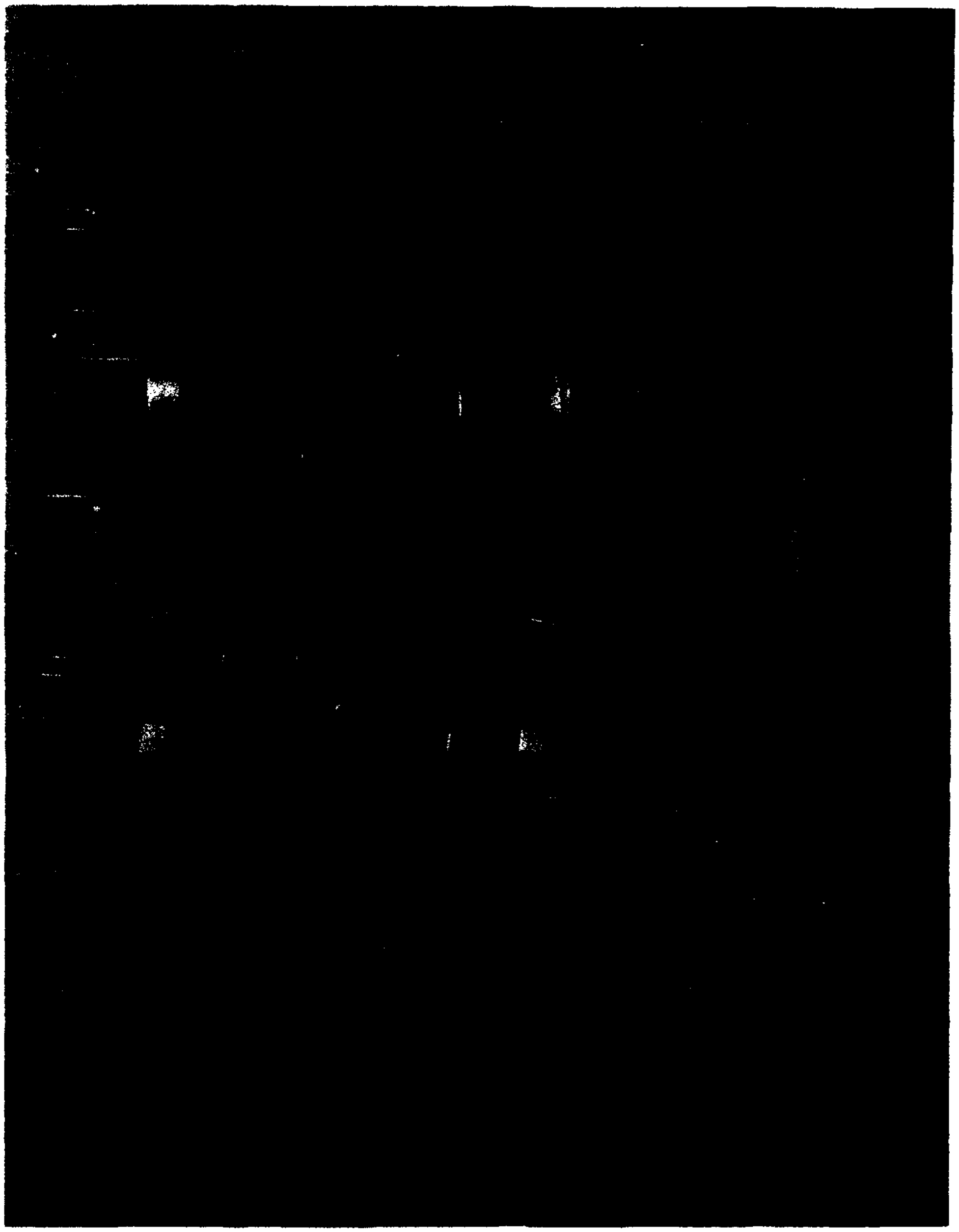
Fig. 3. Ion source with atomic-beam subassembly partially removed.



ZN-2070

Fig. 4. Completely assembled ion source.

positive ion intensity depends not only on the surface concentrations of these decomposing species but also on the temperature-dependent competition between the various possible desorption and decomposition mechanisms. The surface concentration of the contributing molecules depends primarily on the surface concentration of oxygen and fluorine. This in turn is controlled by the temperature-dependent equilibrium balancing of arrival and departure rates of these adsorbed gases, but is complicated by the fact that at our optimum operating pressures most if not all of the arriving oxygen and fluorine diffuses from the interior of the metal, and this again has both a temperature-dependent and a time-dependent rate. Barium also diffuses out of a high-purity tantalum filament, and early in the lifetime of the filament this gives rise to a barium current which is a sizeable fraction of the barium current from the oven.

The interaction with fluorine gives rise to a simultaneous BaF^+ ion current, but no BaO^+ ion current is observed. The interaction with oxygen is detected by the similarity in the behaviors of the Ba^+ and TaO^+ ion currents following a sudden change in temperature and the behavior of the Ba^+ ion current when O_2 is admitted into the system.

We established that the main species arriving at the hot filament from the oven was barium. This was done by measuring the dependence of the high- and low-temperature Ba^+ ion currents and the BaF^+ ion current on the oven temperature. In all three cases this temperature dependence gave a heat of sublimation of 39.0 ± 1.0 kcal/mole, a value consistent with the value published by Stull and Sinke.[27] These curves are shown in Fig. 5. A possible saturation of the surface fluorine can be seen in the curve of BaF^+.

General Discussion

Over a period of 14 days four runs were made. A run consisted of measuring the temperature dependence of the barium ion current from a hot tantalum filament at constant arrival rate of barium atoms. Measurements were made during both increase and decrease of the temperature. At temperatures higher than 2500°K equilibrium was always reached in a time small

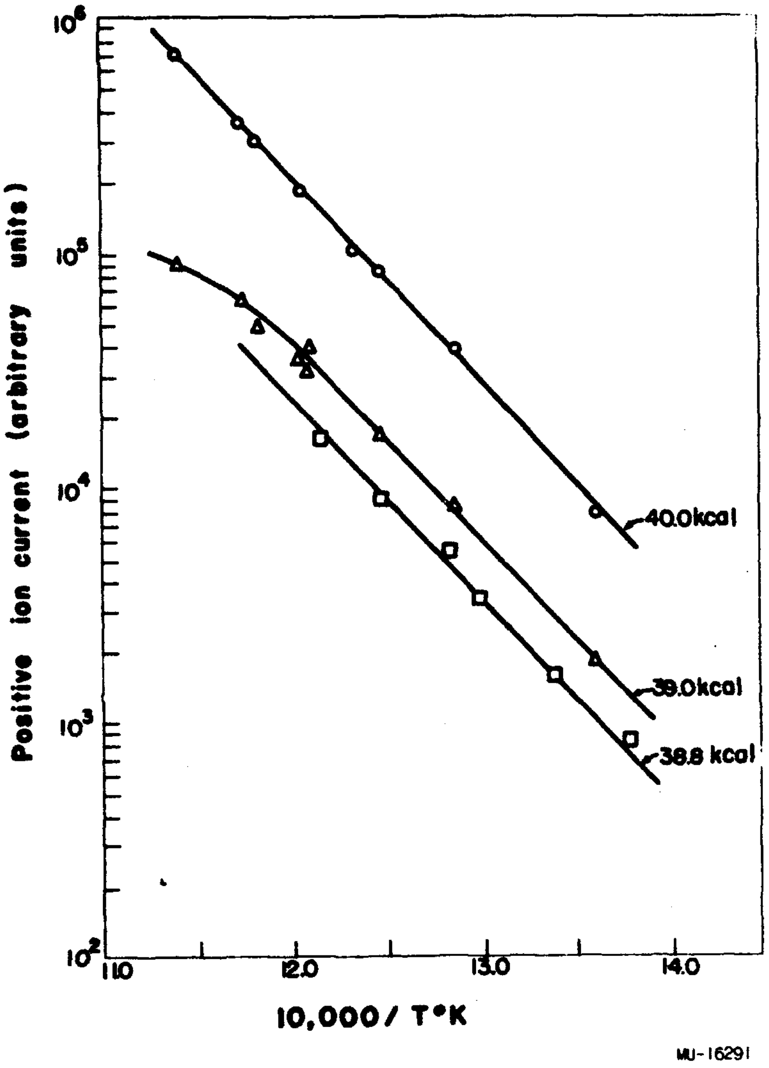


Fig. 5. Dependence of ion current on oven temperature, barium on tantalum.
△ - BaF^+ ionizing filament at 1584°K
⊙ - Ba^+ ionizing filament at 1584°K
□ - Ba^+ ionizing filament at 2189°K.

with respect to the response time of the recording device. At lower temperatures delays in reaching equilibrium were noted. The nature of these delays plays an important part in the interpretation of surface ionization phenomena and is discussed later in detail.

The results of three of the four runs are plotted in Fig. 6. Absolute values of positive ion current are arbitrary but are consistent between runs. The runs are plotted on multiscale semilog paper so that we may more conveniently discuss the aging process of the filament. It should be noted that the difference between the data for increasing and for decreasing temperature lies partially in systematic drifts in the system and partially in determining when equilibrium had been reached. These curves have three more or less distinct characteristics: first, the straight-line region at temperatures higher than 2500°K; second, a broad peak in the region of 2100°K; and third, another broad peak at about 1600°K.

The straight line at temperatures higher than 2500°K represents ionization according to the Saha-Langmuir theory, using a tantalum work function of 4.23 ± 0.03 ev. The broad peak at 2100°K represents the contribution to the barium ion current produced by a chemical interaction with oxygen adsorbed on the tantalum surface. This oxygen comes both from the system and from the interior of the filament. The broad peak at 1600°K represents barium ions produced by a chemical interaction with fluorine atoms adsorbed on the tantalum surface. The fluorine appears to come entirely from the body of the filament.

It is easy to see that essentially all the features of these curves are consistent with these postulations. In the higher temperature region the slope is virtually constant, both with the age of the filament and with the arrival rate. This is precisely what the Saha-Langmuir equation predicts for a clean tantalum surface with constant work function. We also note that the ratio of Ba^+ ions at 2100°K to that predicted by extrapolating the Saha-Langmuir line decreases as a function of time. This is indicative of the gradual reduction in the arrival rate of oxygen at the surface as both the system and filament are cleaned up. That this ratio is not a function of arrival rate of barium atoms is seen from Runs

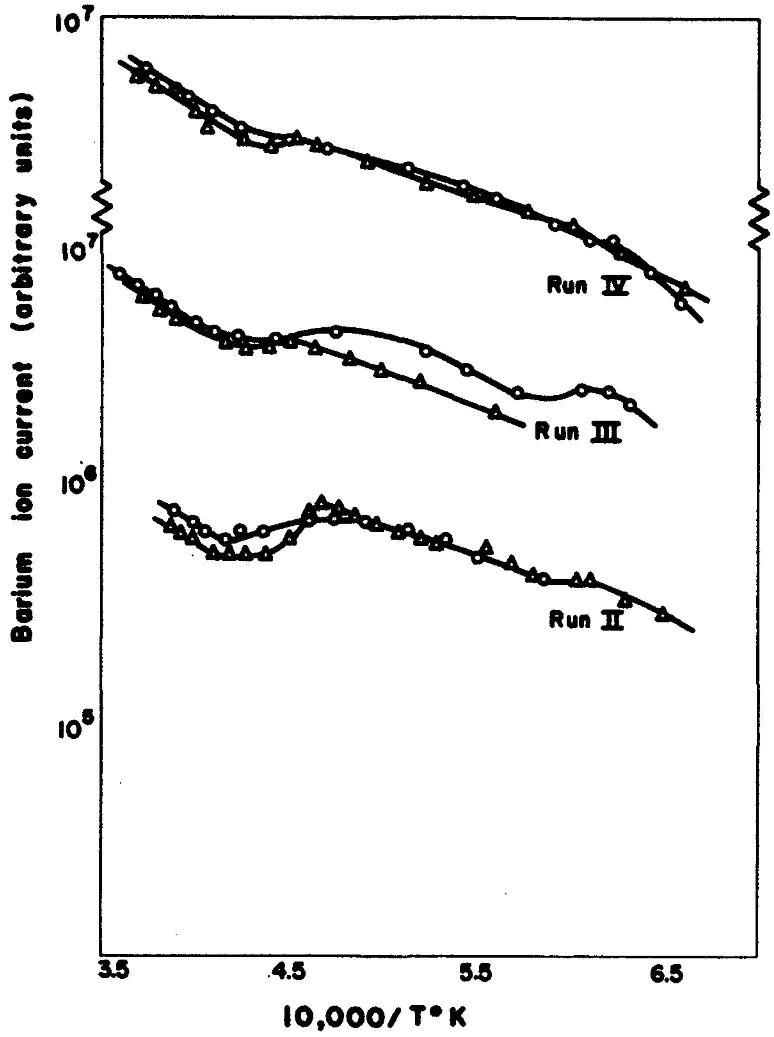


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Fig. 6. Ionization of barium on tantalum.
Δ - Increasing temperature.
⊙ - Decreasing temperature.

II and III, whose arrival rates vary by a factor of about ten. This indicates that the barium-oxygen reaction is not purely oxygen-limited. Essentially the same fraction of the barium atoms reacts with oxygen even though the barium arrival rate is increased by a factor of ten. At this temperature the barium ion current goes to zero essentially instantaneously when the shutter is closed, indicating a very short residence time for barium on the surface. The increase in the barium ion current above that predicted by the Saha-Langmuir theory must then be a measure of the surface coverage of oxygen on the tantalum. We also note that as a function of time the peak attributed to fluorine is decreasing faster than the peak attributed to oxygen. This is partially because the low-temperature side of the oxygen peak is very broad and actually extends under the fluorine peak. In addition essentially all the fluorine is arriving from the interior of the tantalum, whereas the oxygen is being supplied both by diffusion and by condensation from the gas phase, at least during the early part of the runs.

The exact position of the oxygen peak seems to depend on whether the temperature was being increased or decreased at the time the data were taken. This may be explained by the fact that following a sudden increase in temperature there is always excess oxygen on the surface, and following a sudden decrease in temperature there is always less than an equilibrium amount of oxygen on the surface. The natural consequence of taking data a short time before equilibrium is reached is to shift the peak obtained on decreasing the temperature to a slightly lower temperature. This is analogous to having a lower steady-state arrival rate of oxygen at the surface, a condition which is discussed in the following paragraph. In Run IV every precaution was taken to be sure that steady state was reached on each point. It will be seen that the curves are essentially identical, both on increasing and decreasing the temperature.

It is also apparent from Fig. 6 that both the oxygen and fluorine peaks are shifting to lower and lower temperatures as the filament and system age. This is a natural consequence of depleting the oxygen and fluorine concentrations on the surface and in the interior of the filament. The contribution to the barium ion current on the low-temperature side of the peaks is limited by the rate of decomposition and vaporization of the products formed, or perhaps by the amount of barium arriving at the surface. Since we know nothing except by inference, about the efficiency of the decomposition of the products in forming ions it is not possible to say which is actually the limiting factor. On the high-temperature side of the peaks the contribution to the barium ion current is limited by the amount of fluorine present on the surface, which, as we have pointed out, decreases as the filament ages.

We should note again at this point that some of the oxygen and essentially all of the fluorine appear to be coming from the tantalum rather than from the vapor phase of the system. Although the system pressure improved by a factor of about three during the course of the series of runs shown in Fig. 6, we found that the system pressure had to be increased by a factor of about ten with air to make an appreciable change in the barium ion current. The result of letting air into the system was a sudden decrease in the barium ion current, followed by a slow rise to a new higher value. This may be interpreted in terms of reaction of barium with moelcular oxygen to form a loosely bound BaO_2 which does not primarily decompose to form barium ions, but slowly decomposes to form BaO, which in turn decomposes to form barium ions. This interpretation is made by analogy with the uranium-oxygen-tungsten system described later. In this system it was possible to follow the uranium, UO^+, and the UO_2^+ ion currents. It is not possible to say that the higher oxides do not make some contribution to the metal ion current, but it was consistently noted that their contribution was appreciably less than the lower oxides.

The most likely oxygen containing species in the gas phase are O_2, CO_2, and H_2O. It is possible that any one, or all of these species contribute to the surface concentration of oxygen.

Throughout the course of the experiments we were unable to observe a BaO^+ ion current. The relation between the barium ion peak at about $2100^\circ K$ and the oxygen concentration on the surface is indicated in two ways: (a) by the qualitative evidence mentioned earlier that the net effect of letting air into the system is to increase the Ba^+ ion current, and (b) by the quantitative measurements of the rate at which the two ion currents, Ba^+ and TaO^+, come to equilibrium when the temperature is increased. The half life of the controlling mechanism in both cases is the same and has the same temperature dependence. A plot of the half life as a function of $1/T$ gives a straight line with an activation energy of 5.03 ev. This number is probably a measure of the temperature dependence of the rate at which oxygen is being desorbed from the surface, and is possibly the activation energy for the desorption of oxygen from a tantalum surface. These data are shown in Fig. 7.

The fluorine interaction is established primarily by the presence, over the same temperature region, of a BaF^+ ion current, peaking at a temperature very close to that for the barium ion peak attributed to fluorine. This is shown in Fig. 8. The extrapolation of the Saha-Langmuir line to this temperature region, with consideration of the lower volatility of barium, predicts very few Ba^+ ions. This indicates that most of the barium ions are coming from another mechanism. In addition, if the shutter is closed, thus interrupting the atomic beam, the Ba^+ and BaF^+ ion currents drop to zero with approximately the same half life, and those half lives have identical temperature dependences. Also, as for oxygen, the two currents behave similarly following a sudden change in temperature. The equilibrium half lives for the two species are shown in Fig. 9. It should be noted that the effect of oxygen is possibly quite high in the region of the fluorine peak, and until we are able to measure these desorption life-times with much greater accuracy it will be impossible to resolve the various reactions that may be involved.

Figure 10 plotted on the same horizontal scale as Fig. 6, shows rough data indicating the equilibrium time at each hot-filament temperature. The peak in the high-temperature region may be attributed to the oxygen interaction, and the low-temperature rise to the fluorine interaction.

High-Temperature Region

During the course of a given run small nonreproducible drifts in the positive ion current were often observed. This was not surprising,

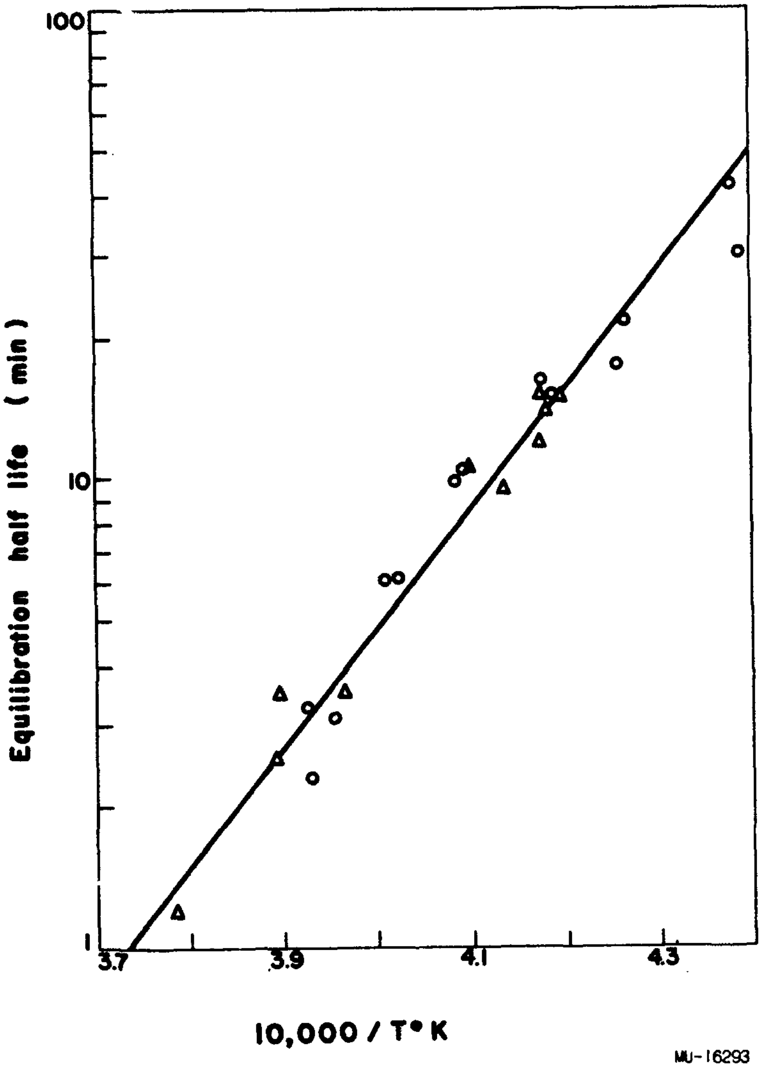

Fig. 7. Rate of equilibration of positive-ion current following increase in temperature.
⊙ - Ba^+ from tantalum surface
▲ - TaO^+ from tantalum surface.

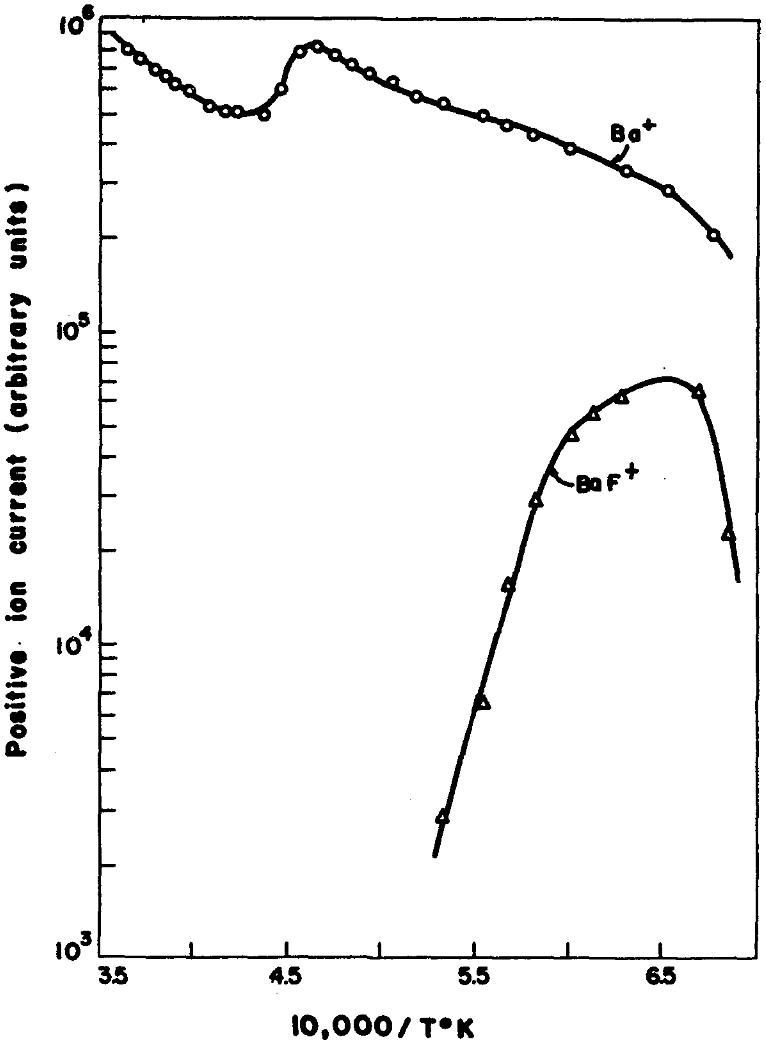

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Fig. 8. Equilibrium ion currents, barium on tantalum.

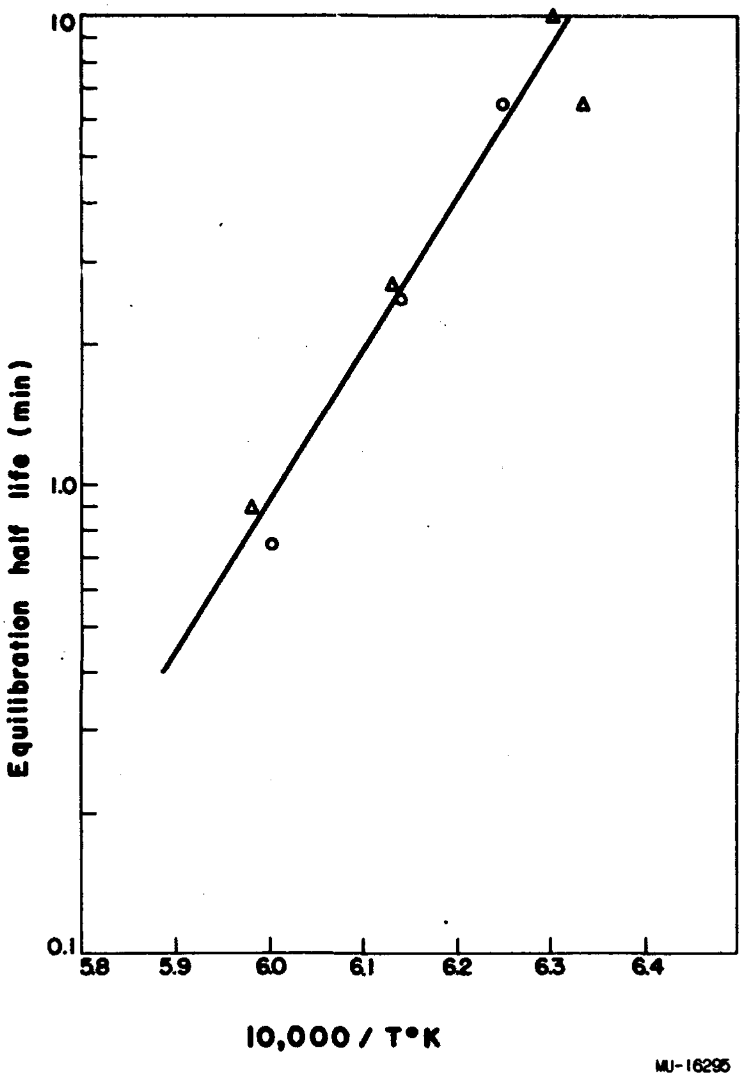

Fig. 9. Rate of equilibration of positive-ion current following increase in temperature.
⊙ - BaF^+ from tantalum surface
▲ - Ba^+ from tantalum surface.

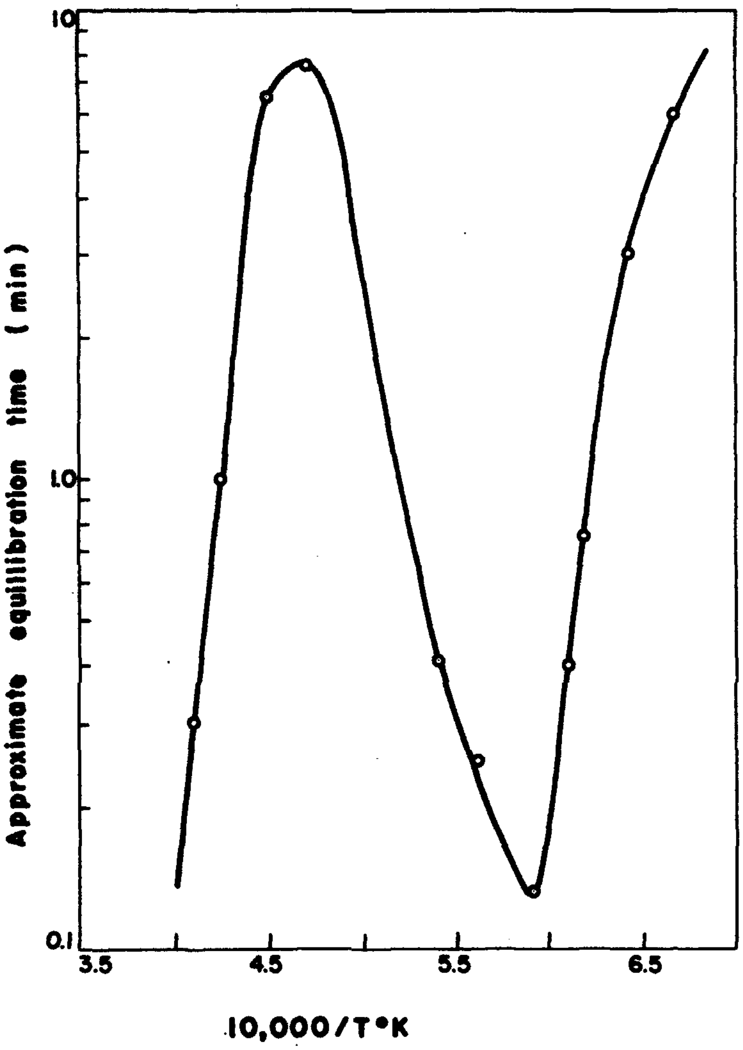

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Fig. 10. Approximate equilibration rate; decreasing temperature; Ba$^+$ ion current on tantalum.

and these drifts, often amounting to as much as 5% of the steady-state current at a given temperature, were almost certainly due to fluctuations inherent in the electronic devices used in carrying out the experiment. Small drifts in the total power input to the sample oven, or in the ion-accelerating potential, could easily account for larger apparent current drifts than those normally noted. In order to get reproducible results it was necessary to devise an experimental procedure that would both eliminate these fluctuations and at the same time allow us to measure the barium ion current from a filament that was sufficiently "clean" that contributions to the ion current from the oxygen interaction was negligible.

This was accomplished in the following manner. It will be noted in Fig. 10 that when the temperature is suddenly decreased the time necessary to reach equilibrium at 2200°K is about 7 minutes, and also at this temperature the total equilibrium deviation from the Saha-Langmuir line is about 6% of the total Ba^+ ion current. At slightly lower temperatures the delay time is much longer. Our procedure was to start at the maximum possible temperature and decrease the temperature stepwise as rapidly as possible. The limiting factor here was the rate at which pyrometric temperature determinations could be made In this manner it was possible to take about ten readings at temperatures higher than 2200°K in about 2 minutes. These data were essentially free of interference from oxygen. In analysis of the data, only absolute changes in current following a sudden decrease in temperature were considered. The value of the ion current just prior to lowering the temperature was corrected to the instantaneous original value at that temperature. In this manner the small, nonreproducible drifts of undetermined origin were in effect eliminated. Care was of course taken that these drifts were nonreproducible and were not part of the system being studied. This procedure was not always necessary, but data treated in this manner always agreed with data for which no drift was noted.

We were able to obtain highly reproducible agreement of the temperature dependence of the barium ion current with that predicted by the Saha-Langmuir theory. A typical run is shown in Fig. 11. The activation

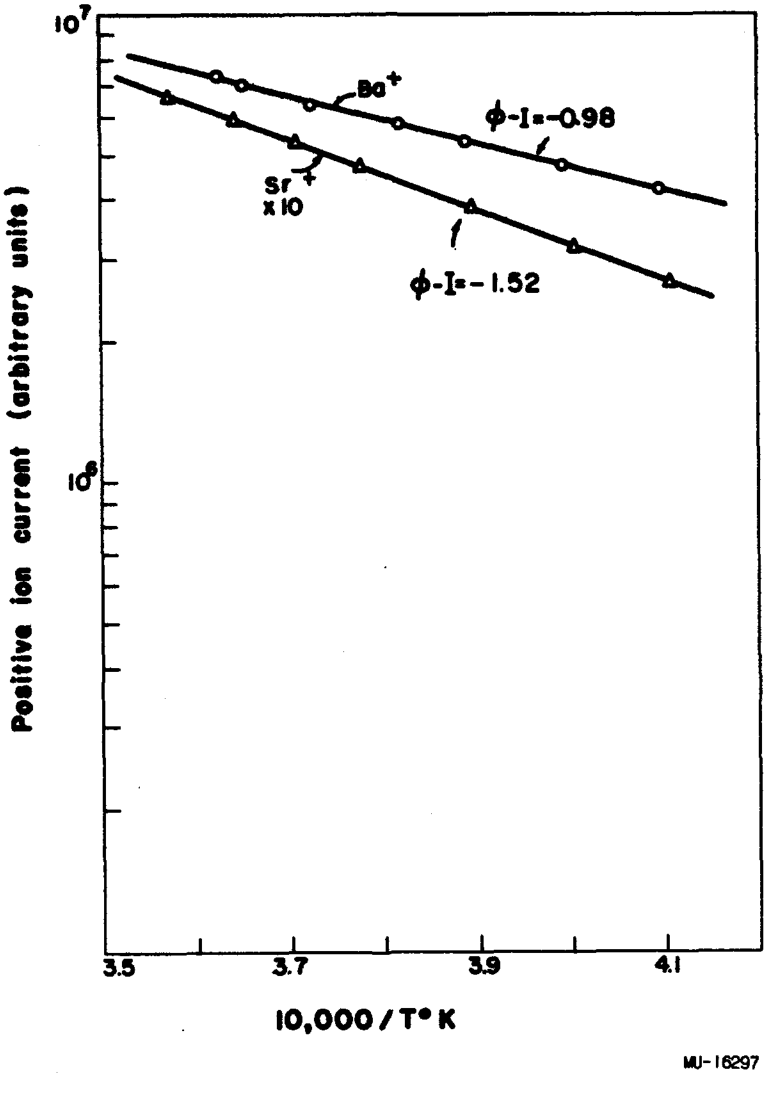

Fig. 11. Ionization of barium and strontium on tantalum; high-temperature region. Note: Vertical positioning of the two currents is arbitrary.

energy obtained was 0.98 ± 0.03 ev. Using 5.21 ev as the ionization potential of barium, we obtain 4.23 ± 0.03 ev as the work function of tantalum. This value is consistent with the 4.19 ev value reported by Fiske[26] and with our own value of 4.21 ev obtained from electron-emission experiments made on a different filament from the same stock of ribbon. This value apparently substantiates the Saha-Langmuir theory for the barium-tantalum system.

THE IONIZATION OF STRONTIUM ON TANTALUM

During the course of the runs investigating the ionization of barium on tantalum it was noted that the trace impurity of strontium in the barium was producing a detectable ion current. The strontium current was less than the barium ion current by several orders of magnitude, but it was possible to get reasonably good data at high temperatures. Since the ionization potential of strontium is about 0.5 ev higher than that of barium, the ionization efficiency is much lower. This, combined with the fact that there was very little strontium in the system, prevented measurements in the low-temperature region. We were unable to detect any SrF^+ ion current. However, if it existed and if it had roughly the same relation to the Sr^+ ion current as the BaF^+ ion current had to the Ba^+ ion current, it would have been undetected.

High-Temperature Region

The strontium data at high temperatures were taken in exactly the same manner as described earlier for barium. Only two runs were made after the system cleaned up, and one of these was taken simultaneously with a set of barium data which deviated markedly from all other sets.

The one good set of data indicates that the high-temperature surface ionization of strontium is in agreement with the predictions of the Saha-Langmuir theory. An activation energy of 1.52 ev was obtained, yielding a work function for tantalum of 4.17 ev. This is based on the 5.69 ev ionization potential of strontium reported by Moore.[28] This value is slightly lower than the value obtained with barium, but is in essential agreement. The experimental data in the high-temperature region are shown in Fig. 11.

THE IONIZATION OF BARIUM ON TUNGSTEN

Our experiments on the ionization of barium on tungsten disagree with the work of Guthrie,[15] but are in qualitative agreement with the work of Morosov.[16] Guthrie obtained a high-temperature slope of zero, which is not consistent with the predictions of the Saha-Langmuir theory. Morosov obtained a high-temperature slope of 0.39 ± 0.06 ev, in contrast to the theoretical slope of about 0.6 ev. He notes that slightly improved agreement is obtained by treating the data according to Darwin and Fowler's modification[28] of the Saha-Langmuir theory. This modification takes into account the excited states of the barium ion and atom. In addition, Morosov noted unexpectedly high ionization efficiencies at low temperatures, but attributed these to a change in the electronic work function of tungsten due to adsorption of oxygen at low temperatures.

In contrast with these results we find, after resolving out the effect of the chemical reactions which become predominant at lower temperatures, that the high-temperature slope agrees with theory. We obtain 0.60 ± 0.01 ev for the activation energy. Using the value of 5.21 ev for the ionization potential of barium gives 4.58 ± 0.01 ev. (A small correction amounting to 0.03 ev, must be made because of the relatively high ionizing efficiency.) This value is quite consistent with the generally accepted values for the work function of tungsten.[30] We also observe the low-temperature maximum in the barium ion current, but attribute this phenomenon to an independent ionization mechanism associated with the same type of chemical reactions as noted in ionization on tantalum. The enhancement of the barium ion current by an interaction with fluorine is accompanied by a BaF^+ ion current, as for tantalum. While there are indications that an oxygen interaction contributes to the low temperature peak, we were unable to substantiate this except by comparison with the uranium and neodymium studies made later. Only at very high temperatures were we able to see a WO^+ ion current. In the temperature region where BaF^+ was important we were unable to find any ionizing species containing oxygen that could have been used to check the oxygen desorption rate. This is consistent with the high volatility of tungsten oxide, which would tend to remove oxygen much more rapidly than in the case of tantalum. However, the peak of this oxygen effect occurs at the same temperature as a UO_2^+ ion current peak and a NdO^+ ion current peak noted in systems described later. Early in the series of runs on a single filament we noted a small barium interaction in the high-temperature region. This region later became essentially a straight line. This interaction occurs in the same temperature region as the UO^+ ion current peak in the uranium-tungsten system. It is possible that these two effects can be attributed to interactions of barium with atomic and molecular oxygen, as is discussed later for uranium.

General Discussion

Figure 12 shows four of the many runs made with barium atoms impinging onto a hot tungsten filament. The runs are numbered in chronological order. They are plotted on multiscale semilog paper to show the general effect of cleaning up the filament and the system. Run I was made after about 5 hours of outgassing the filament at 2000°K. Run III was made the following day after about 4 additional hours of heating at 2200°K. Runs IV and V were made 1 week later, following many hours of operation at various temperatures in addition to outgassing for periods of at least 1 hour at 2500°K and 2700°K and for brief periods at 2900°K. No precise history of this period was recorded, but the filament had aged to the extent that any changes in emissive properties were imperceptibly slow.

Several general characteristics of the curves are noted at once. Each contains a relatively straight-line region at high temperatures as predicted by the Saha-Langmuir theory. It is noted that in Run I this line is not straight. It is this perturbation which may possibly be attributable to the interaction of barium with atomic oxygen.

At lower temperatures there is a peak in the Ba^+ ion current, which in the final run has a value about ten times the current predicted

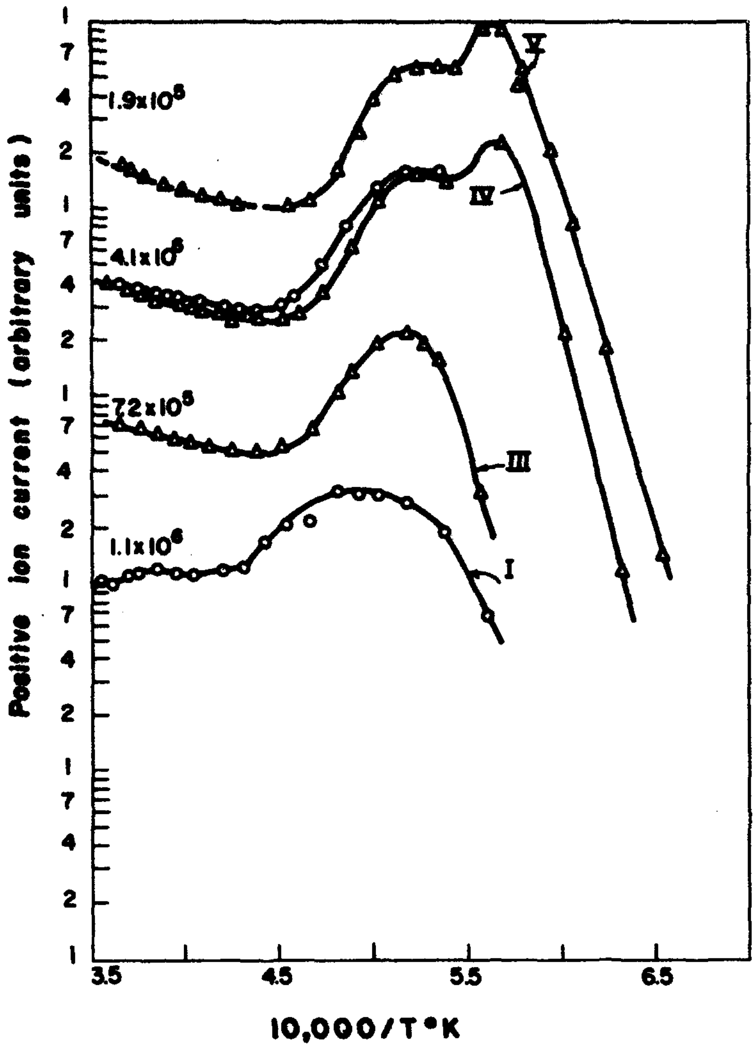

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Fig. 12. The ionization of barium on tungsten.
△ - increasing temperature
○ - decreasing temperature.

by extrapolating the Saha-Langmuir line to the temperature of the peak maximum. The Saha-Langmuir theory predicts an ionization efficiency of 6.25% at 2500°K for barium on tungsten, If this efficiency is realized, the ionization efficiency at the maximum of the low-temperature peak in the final run is about 30%. It is noted that both the position of the maximum of the peak and the extent of the straight-line portion of the curve move to lower and lower temperatures as a function of filament aging.

An empirical resolution of the two sections of the curve indicates that the high-temperature straight-line portion of the curve is representative of the Saha-Langmuir theory, but that the low-temperature peak, which is attributable to chemical interactions, contributes to the slope in such a manner that the apparent unresolved slope is somewhat lower than the slope predicted by theory. Upon resolution of the low-temperature effects the slope is in excellent agreement with that predicted by the Saha-Langmuir theory. The empirical resolution consists of extrapolating the apparent slope at high temperatures into the lower-temperature region. By difference, the shape of the low-temperature curve is obtained as a first approximation, and the extent to which it contributes to the high-temperature slope is determined by extrapolation. The process is repeated several times until the high-temperature slope is no longer changed. Figure 13 shows a set of resolved data.

It is noted in Fig. 14 that the Ba^+ ion peak appears to be a composite peak representing Ba^+ ions from two sources. The relationship between the low-temperature portion of this peak and fluorine is established by comparison with a BaF^+ ion peak which occurs at the same temperature. On the low-temperature side of the peak the Ba^+ and BaF^+ ion currents equilibrate with the same half life when the temperature is changed, indicating that their formation is dependent on the concentration of the same species on the surface. The high-temperature portion of this peak is due to an interaction with oxygen. This is established by the fact that UO_2^+ and NdO^+ ion peaks are observed at exactly the same temperature in the uranium-tungsten and neodymium-tungsten systems discussed later. As noted above, we were unable to detect an oxygen containing species in the barium-tungsten system, except for a small WO^+ ion current at very high temperatures.

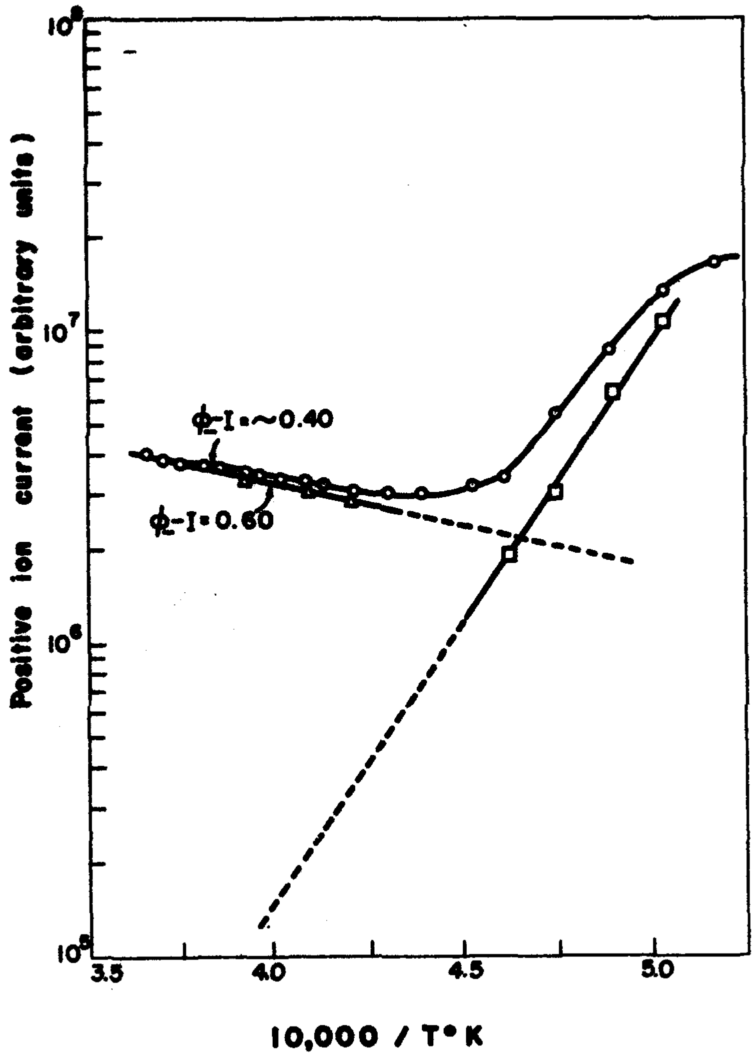

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Fig. 13. Empirical resolution of Ba^+ current into high-temperature straight line and lower-temperature chemical effect.

O - Ba^+ experimental data
□ - Ba^+ from chemical reactions
Δ - Ba^+ from high-temperature straight line.

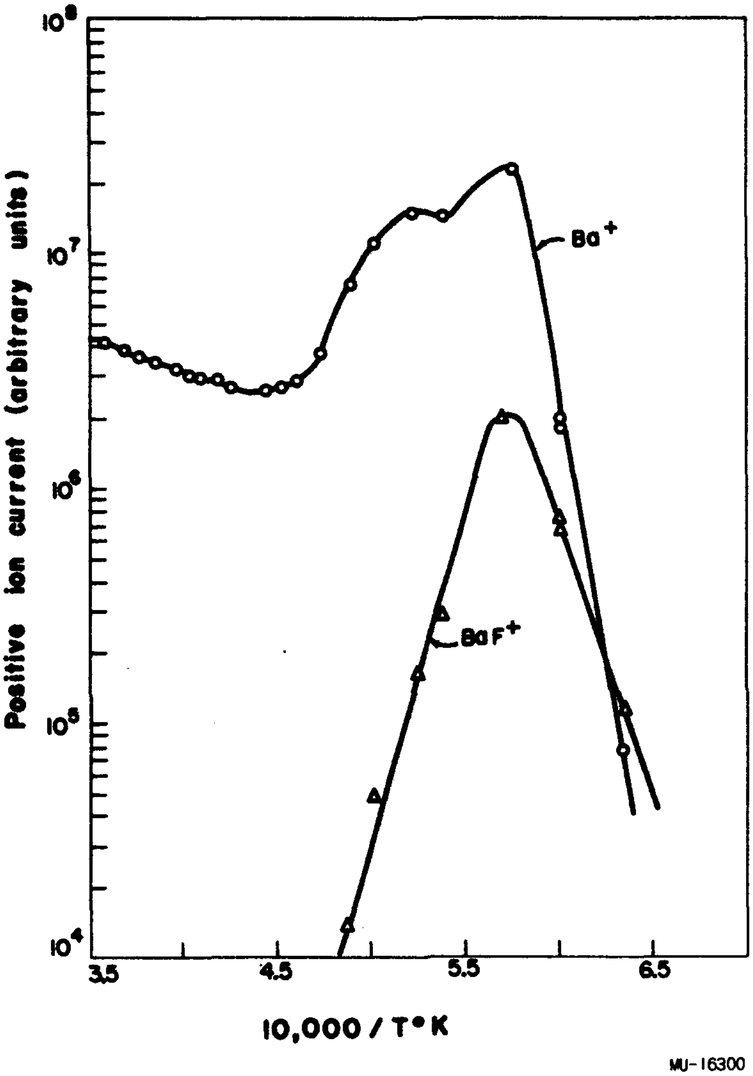

Fig. 14. Equilibrium ion currents, barium on tantalum.

High-Temperature Regions

At the time the barium-tungsten ionization experiments were run the rapid experimental techniques used in the barium-tantalum and the barium-rhenium systems had not been devised. Because of the length of time necessary to outgas the system thoroughly and because of the excellent agreement with theory obtained by resolving the two parts of the experimental curve, the experiment was not repeated.

We found that at temperatures higher than about 2500°K the slope of the approximately straight line is in excellent agreement with the predictions of the Saha-Langmuir theory. The slope before and after resolution of the two effects is shown in Fig. 13. In Table I we have tabulated the experimental and the resolved slopes for the runs made after reasonable aging of the system and filament. We obtain a value of 0.60 ± 0.01 ev for the activation energy. The theoretical value of this slope, calculated from the Saha-Langmuir theory, taking into account the fact that from 3% to 6% of the barium is ionized, is approximately 0.6 ev, based on a tungsten work function of 4.58 ev. It should be noted that this line is straight only to a first approximation, owing to the relatively high ionization efficiency.

Table I

Run number	Experimental Slope - ev	Corrected Slope - ev
III - (Increasing temperature)	0.48	0.59
IV - (Increasing temperature)	0.56	0.60
IV - (Decreasing temperature)	0.40	0.60
V - (Increasing temperature)	0.61	0.61

THE IONIZATION OF BARIUM ON RHENIUM

There is no well-accepted value of the gross thermionic work function of rhenium. Values appearing in the literature vary from about 4.6 to 5.2 ev.[31] In the series of experiments reported here we find that the ionization efficiency of barium on rhenium is essentially constant above temperatures of 2300°K, indicating a work function for rhenium very close to or appreciably greater than the 5.21 ev ionization potential of barium. The approximately 5.21 ev value is substantiated by the work with the strontium-rhenium system discussed in the next section. In the lower-temperature regions the barium-rhenium system is qualitatively similar in behavior to the barium-tungsten and barium-tantalum systems. Two factors, however, contribute to giving the curves a somewhat different appearance. First, because of the relatively high work function of rhenium, a large fraction of the barium is ionized by the Saha-Langmuir process. For this reason the low-temperature-region chemical interactions cannot add greatly to the total ionization efficiency. Second, the rhenium filaments were found to have appreciably higher impurity levels. This resulted in a greater number of interactions in this system, with the accompanying added difficulty in resolving and identifying these reactions. Fluorine and chlorine reactions were identified and other reactions were noted but not identified. There is unquestionably an oxygen effect, but as with tungsten this was impossible to identify directly because of the ansence of a measurable BaO^+ or ReO^+ ion current.

General Discussion

Figure 15 shows a typical barium-rhenium run. Curve I shows the equilibrium values for the Ba^+ ion current. At high temperatures this curve is seen to have a negative slope of about 0.1 ev. This equilibrium slope apparently reflects a change in the barium-ionization efficiency, brought about by a chemical interaction of undetermined nature. It should be emphasized that the points of Curve I represent equilibrium points. Following a sudden dropping of the temperature between these points there was no measurable change in the Ba^+ ion current. This was followed by a slow, reproducible decrease in the ion intensity over a period of several minutes. The Ba^+ of Fig. 16 shows data taken during rapid decreases in temperature and corrected for this drift in a manner similar to that described for the high-temoerature barium-tantalum system. This drift is almost certainly due to a chemical interaction similar to those described

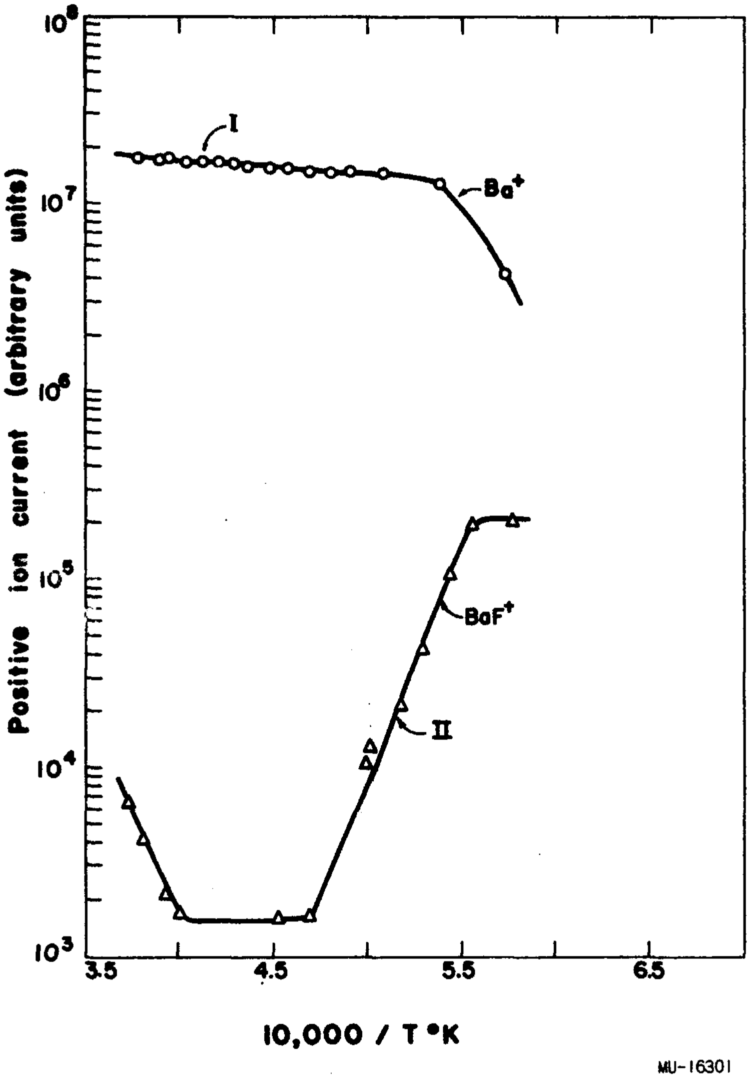

Fig. 15. Equilibrium ion currents, barium on rhenium.

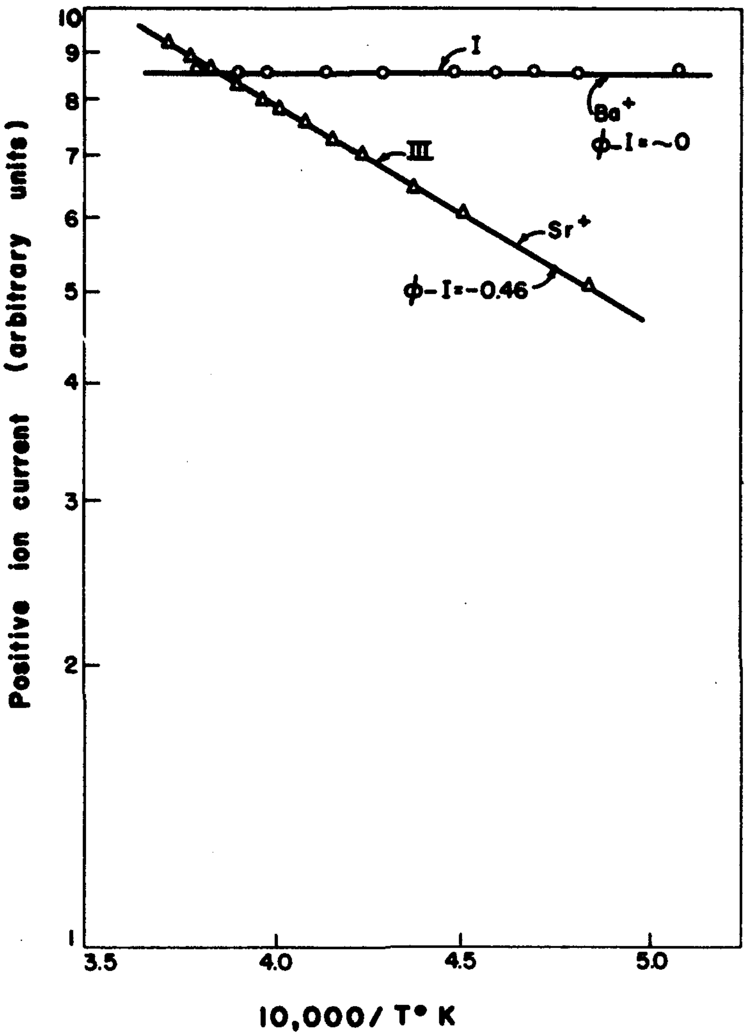

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Fig. 16. Ionization of barium and strontium on rhenium; high-temperature region. Data corrected for drifts. Note: Vertical positioning of the two curves is **arbitrary.**

earlier. In the barium-tantalum system a similar drift was noted at slightly lower temperatures, but the net effect was to increase the barium ion current. In the barium-rhenium system the net effect is to slowly decrease the Ba^+ ion current after an instantaneous decrease in temperature. This slow decrease probably results from a change in the surface concentration of some species, which decreases the Ba^+ ion current. Our first thought is oxygen, but we were unable to find any oxygen-containing surface ions with which to check this idea. A careful check of the behavior of the potassium ion current from the filament indicated that following a sudden change in temperature the K^+ ion current equilibrated in a time which was approximately the same as that required for the equilibrium of the Ba^+ ion current. The small absolute value of these changes combined with small unavoidable drifts in the Ba^+ ion current prevented us from obtaining good data in this experiment.

On increase of temperature the K^+ ion current increases rather sharply, then decreases slowly to a slightly lower value. Recalling that on increase of temperature the Ba^+ ion current showed no instantaneous change, but gradually increased in value, one can postulate an interaction between the barium and potassium on the surface. A search for the barium-potassium interaction would involve accurately measuring the half life and the temperature dependence of the half life for the equilibration of the Ba^+ and the K^+ ion currents. As noted above we were not able to make accurate measurements of these half lives. A careful check was made for a BaK^+ ion current but none was found.

An interaction of barium with a strong electropositive adsorbed atom might be expected to decrease the barium ion current, since the interactions with electronegative oxygen, fluorine, and chlorine were seen to increase the Ba^+ ion current.

Curve II, Fig. 15 shows the BaF^+ ion current. This current behaved in a manner identical to that of the BaF^+ ion currents observed on tantalum and tungsten. Because of the lack of structure in the barium ion current it is difficult to make any quantitative comparisons between the two curves. As noted earlier, a $BaCl^+$ ion current was observed. This current was observed before the filament had aged and was no longer observed when the data of Fig. 15 were taken.

High-Temperature Region

The essentials of the high-temperature region were described in the preceding section. It is sufficient to add at this point that except at the very highest temperatures attained a surface chemical interaction interferes with observation of ionization by the Saha-Langmuir process. The effect of this interference is to give an apparent slope somewhat more negative than the true slope, which can be obtained by sweeping very rapidly through the temperature region of interest.

Curve I in Fig. 16 is quite representative of the high-temperature data taken in this manner. There is essentially no temperature dependence of the ion current in this region. From a series of three such runs we obtain an activation energy of 0.0 ± 0.02 ev, indicating a work function for aged rhenium of 5.21 ± 0.02 ev.

The high temperature increase in the BaF^+ ion current indicated in Fig. 15 is caused by BaF diffusing from the interior of the filament. This current is not affected by interupting the atomic beam with the magnetic shutter.

THE IONIZATION OF STRONTIUM ON RHENIUM

The ionization of strontium on rhenium follows much the same pattern as does the ionization of barium on rhenium. However, since strontium is not so efficiently ionized as barium by the Saha-Langmuir process, the low-temperature chemical interactions show a more marked effect. In general we find that at high temperatures a straight line is obtained. The slope of this line is consistent with a rhenium work function of 5.17 ± 0.02 ev in agreement with the value indicated by the work with barium on rhenium.

In the lower-temperature regions a Sr^+ ion peak is obtained. As in the previously discussed work with barium, this peak has associated with it a SrF^+ ion current which peaks at essentially the same temperature.

General Discussion

Figure 17 shows a typical set of data for the ionization of strontium on rhenium. The SrF^+ ion current is also shown. As in the other cases studied, the high-temperature region produces a straight line as predicted by theory. The data were not extended to lower temperatures because of the extremely long time delay involved in reaching equilibrium. It is noted particularly that the SrF^+ and the low temperature Sr^+ ion current peaks occur at more nearly the same temperature than do the Ba^+ and BaF^+ peaks in ionization on tantalum or tungsten. This apparently indicates less interference of the oxygen interaction, which appears to be of considerably less importance for strontium on rhenium than in the other cases. It is not possible to say whether it is because of the strontium or the rhenium that the oxygen appears to be of less importance since the strontium ion current on tantalum was not large enough to study, and since the barium ionization by chemical interaction on rhenium constitutes a relatively small fraction of the total ion current.

High-Temperature Region

Figure 16, Curve II shows high-temperature strontium-rhenium ionization data. These data were obtained in the same manner as the high-temperature data for barium on tantalum. Three runs give a value of 0.52 ± 0.02 ev for the activation energy, indicating a work function for rhenium of 5.17 ± 0.02 ev, a value in reasonable agreement with the value obtained with barium.

As in the barium-rhenium system, the high-temperature increase in the SrF^+ ion current is caused by diffusion from the filament.

THE IONIZATION OF URANIUM ON TUNGSTEN

The ionization of uranium on tungsten appears to follow the Saha-Langmuir theory at high temperatures. At lower temperatures the system undergoes the type of chemical interaction noted in the previously discussed systems. It is significant that, of the seven systems investigated,

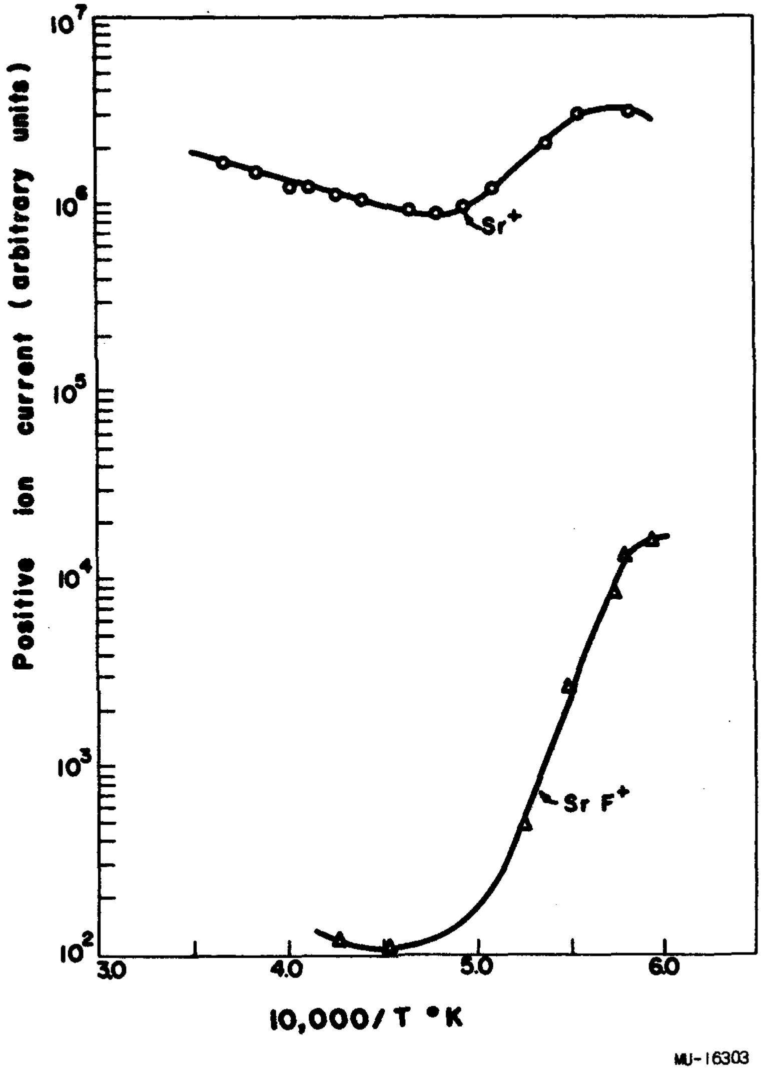


Fig. 17. Equilibrium ion currents, strontium on rhenium.

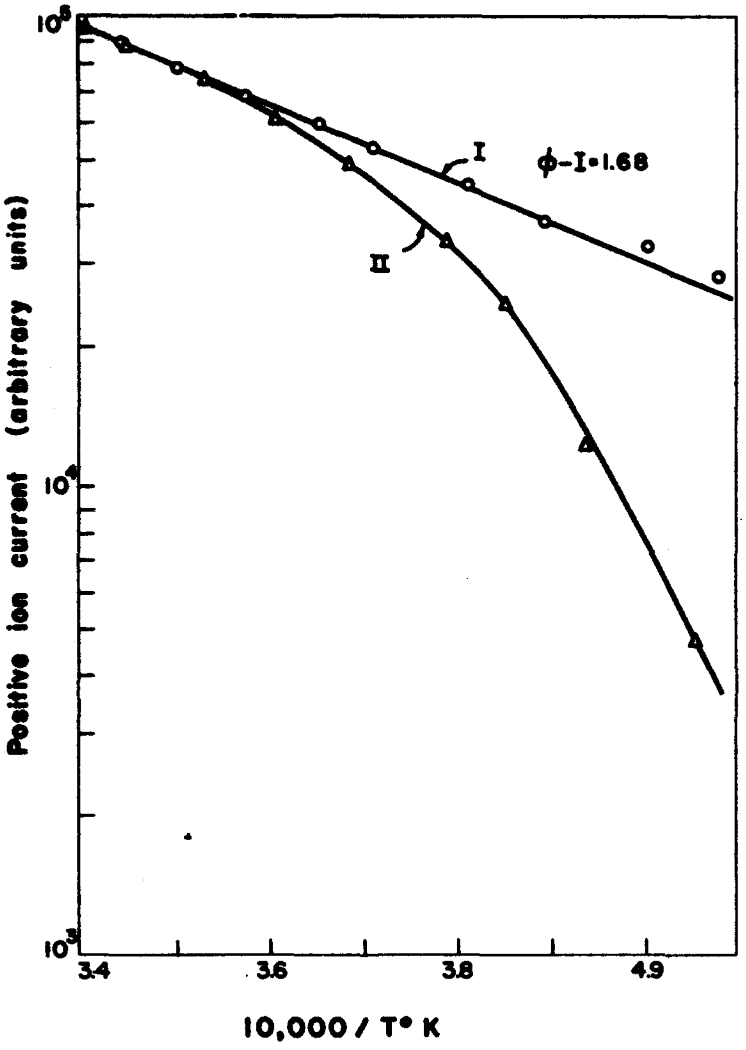
the uranium-tungsten and the neodymium-tungsten systems are the only ones that show a marked dependence on pressure of the system in the region from 1×10^{-7} to 1×10^{-6} mm Hg. This pressure dependence was particularly noticeable in the lower-temperature regions, and showed up in the marked change in the shape of the curves of the uranium ion current as a function of time during the course of a given day's running. As a given run progressed and the oven was outgassed the entire source end of the machine gradually warmed up and the pressure rose slowly through the region mentioned above. At the start of each run we were unable to detect any uranium oxide ion currents. However, by the end of the run, when the pressure had risen to about 8×10^{-7} mm Hg, large UO^+ and UO_2^+ ion currents were noted. We were also able to induce these oxide ion currents early in the course of a given run by passing excess power through the solenoids that operated the magnetic shutter. Outgassing of the coils caused a tenfold pressure rise in the source region in about 10 seconds. The effect of this pressure rise on the U^+, UO^+, and UO_2^+ ion currents was qualitatively identical to the effect caused by the gradual warming and outgassing of the system. The effect of letting air into the system was again qualitatively similar. In this case it was possible to note specifically that both the U^+ and UO^+ ion currents dropped when air was admitted. The U^+ current dropped much more than the UO^+ current. There was a simultaneous increase in the UO_2^+ ion current. At no time were we able to detect a UF^+ ion current or any other effect that could be attributed to a fluorine interaction.

The slope of the straight line at high temperatures was not markedly affected by increasing the pressure of the system, although the lower limits of linearity were increased appreciably. The slope of this line at high temperatures gives an excitation energy of 1.67 ± 0.02 ev for the uranium ionization. With a tungsten work function of 4.58 ev this gives an ionization potential for the uranium atom of 6.25 ± 0.02 ev.

This value does not agree with the one reported by Keiss, Humphries, and Laun.[32] From the fact that uranium is easily ionized in electric arcs and magnetic fields, and also that the short-wave spectrum does not extend below 2900 A., they conclude that the ionization potential of the neutral uranium atom is approximately 4 electron volts. Neither does this work agree with the surface ionization value of approximately 4.7 ev reported by Rauh.[33] His work was similar to the present work in principle, but was done without the aid of a mass spectrometer. The 6.25 ev ionization potential for uranium is in excellent agreement, however, with our semi-quantitative observations on the absolute ionization efficiency. This value of the ionization potential predicts an absolute efficiency which is in reasonable agreement with that observed. The lower values predict net ion currents much larger than those observed.

General Discussion

Figure 18, Curve I, shows a typical set of uranium ion current data at the start of a series of runs. During this run the pressure in the source region varied from about 1.0×10^{-7} to about 8.0×10^{-7} mm Hg. Near the end of the run the data shown in Fig. 19 were taken. The source had been allowed to heat and the pressure in this region had risen to about 6×10^{-7} mm Hg. The exact shapes of the curves and the relative heights of the peaks are not significant, since the pressure continued to change slightly as the run was being made. As noted above, this same effect could be produced by admitting air into the system or by outgassing the solenoid coil. Although the exact mechanism of the reactions taking place was not determined it was quite clear that an equilibrium was being set up between U^+, UO^+, and UO_2^+, and that as more oxygen was admitted to the system the equilibrium was shifted to the higher oxide. On the basis of our experiments it is not possible to determine whether the UO^+ was formed by the decomposition of UO_2 or by the reaction of U with O. However, it is unlikely that the ionization potential of UO is sufficiently low that we would have seen this large number of ions from a process similar to the Saha-Langmuir process. For this reason it is probable that the UO^+ ions are being formed, in part at least, as a decomposition product of a higher oxide, probably UO_2. The source of the UO_2^+ ions is also open to question. It is again quite unlikely that their ionization



MU-16304

Fig. 18. Ionization of uranium on tungsten.
I. Initial run on starting up cold system.
Source pressure = ~1.0 x 10^{-7} mm Hg.
II. Data taken after heating and outgassing of source region had raised pressure to ~6.0 x 10^{-7} mm Hg.

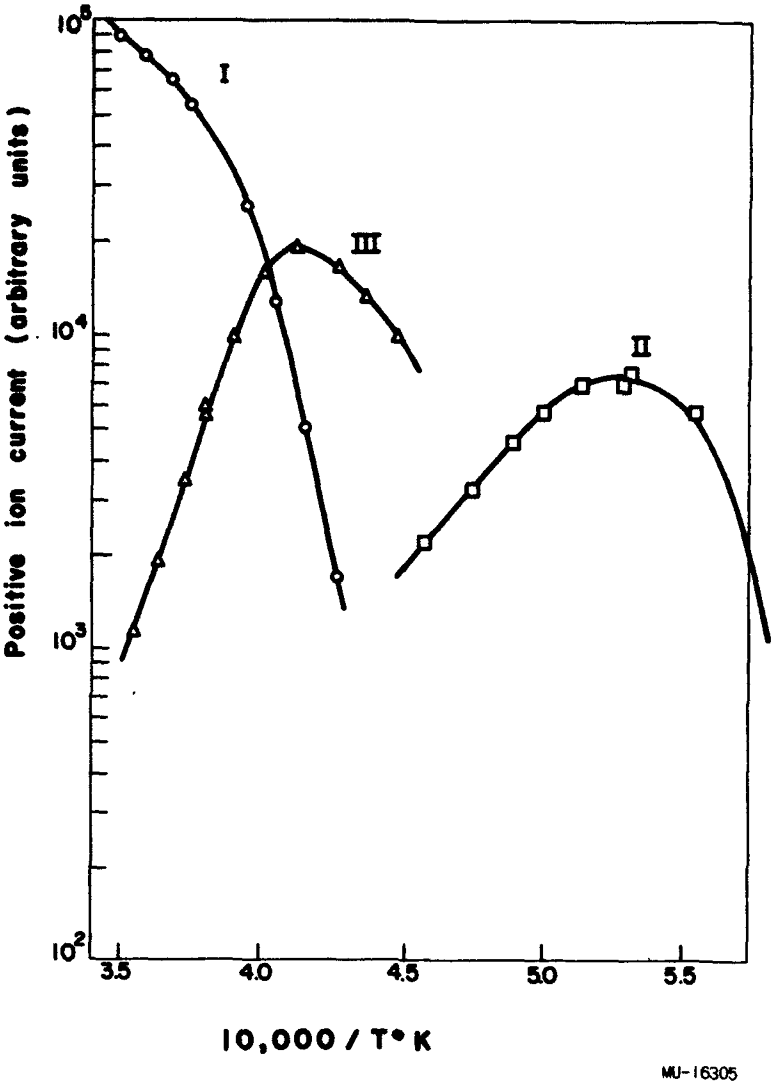


Fig. 19. Ionization of uranium on tungsten. Oxygen effect data taken as pressure of system slowly increased.
I. U$^+$ ion current; taken first; limiting slope gives uranium ionization potential of 6.21 ev.
II. UO$_2^+$ ion current; taken second.
III. UO$^+$ ion current; taken last; pressure up by a factor of two from Curve I.

can be explained on the simple basis of evaporation competition between ions and molecules. This would infer that they were also the products of a decomposition reaction. We feel that many of these questions can be answered by the techniques employed in this research, but that adequate measures must be provided to insure constant control of pressure, and techniques must be developed for measuring very short life times on the surface. We were unable to determine, for example, whether the UO^+ and UO_2^+ ion currents decreased to zero with the same half life after closing of the shutter because the pressure continues to drift slightly as these measurements are being made. In addition only half lives of a limited range could be measured with our recording device. Extremely fast and accurate counting techniques will allow the resolution of complex desorption mechanisms, and allow a more meaningful interpretation of the data presented here.

In order to establish that we were not building up an appreciable fraction of a monolayer of uranium on the tungsten surface, the following experiment was performed. The hot filament was cooled to room temperature and the atomic beam was collected for ten minutes. The natural uranium collected in this manner was recovered from the filament and spiked with a known amount of U^{235} enriched uranium. Analysis of this mixture by the usual isotopic dilution techniques indicated that about 10^{-3} monolayers of uranium had been collected. It is reasonable to assume that the surface concentration of uranium on the hot filament under steady state conditions was many orders of magnitude lower.

High-Temperature Region

Figure 18 shows high-temperature uranium ion current data taken in the rapid manner described in the barium-tantalum discussion. Curve I shows data taken early in the run, under conditions such that no oxide ion currents were observed. Curve II shows data taken later in the run after the oxide ion currents had become quite pronounced. At sufficiently high temperatures the pressure is seen to have no appreciable effect on the slope of this line. The analysis of nine runs of this type give a value of the activation energy of 1.67 ± 0.02 ev. If a tungsten work function of 4.58 ev is used this yields a value of 6.25 ± 0.02 ev for the ionization potential of uranium.

THE IONIZATION OF NEODYMIUM ON TUNGSTEN

The ionization of neodymium on tungsten is very similar to the ionization of uranium on tungsten. At high temperatures the neodymium-tungsten system appears to follow the Saha-Langmuir theory. At lower temperatures the Nd^+ ion current drops below the value predicted by extrapolation of the high-temperature straight line, and a NdO^+ ion current appears. No NdO_2^+ or NdF^+ is observed. The effects of gradually warming the system, outgassing the solenoid coils, or admitting air were qualitatively identical to those observed with uranium, with the noted exception pertaining to NdO_2^+.

As with uranium, the low-temperature reactions did not markedly affect the high-temperature slope. The slope of this line at high temperatures gives an activation energy of 0.52 ± 0.04 ev, which yields a value of 5.10 ± 0.04 ev for the ionization potential of neodymium.

This value does not agree with the 6.31 ev value reported by Moore[34] nor does it agree with the 5.5 ev value reported by Johnson, Hudson, and Spedding.[35] The former represents a value "determined experimentally, but not yet confirmed by series". The work of Johnson, Hudson, and Spedding was identical in principle to the work reported here, but the highest temperature on which their number is based was about 2500°K. We were unable to obtain reproducible results below 2500°K, but the slopes we did obtain were always more negative than the constant slope noted above about 2600°K. This effect is shown in Fig. 20, and it indicates that the Johnson, Hudson, and Spedding data were probably affected by the oxygen interaction noted above.

General Discussion

Figure 20 shows typical sets of Nd^+ and NdO^+ ion current data. As for uranium, the exact shape of the curves is not significant, because the pressure was slowly increasing during the run. The data, however, are sufficiently significant to allow comparison with the uranium data shown in Fig. 19. The NdO^+ ion current peak appears to be a composite peak representing NdO^+ ions produced by at least two mechanisms. It is,

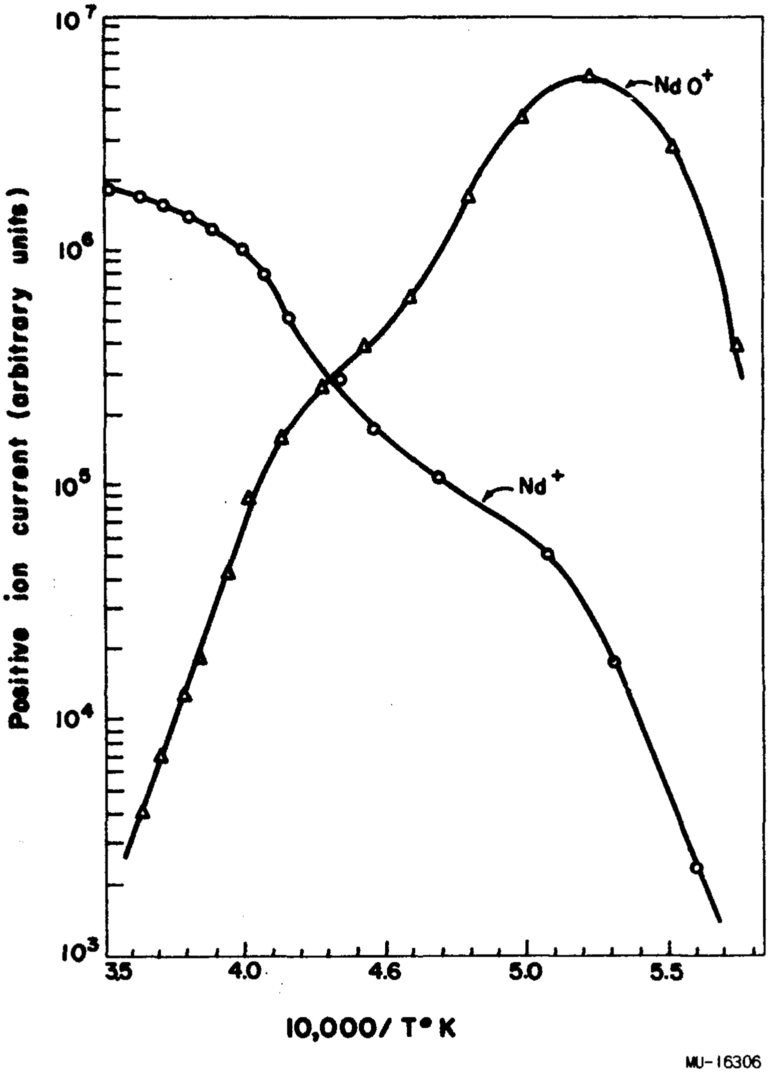


Fig. 20. Ionization of neodymium on tungsten.
△ - NdO^+ from tungsten
O - Nd^+ from tungsten.

in fact, quite similar to what one could construct by increasing the intensity of the UO_2^+ curve in Fig. 19 and adding it to the UO^+ curve in the same figure. The high-temperature side of the NdO^+ peak is very similar to the high-temperature side of the UO^+ peak. The maximum of the NdO^+ peak occurs at the same temperature as the maximum of the UO_2^+ peak. It should also be noted that the maximum of the peak attributed to oxygen in the barium-tungsten system occurs at the same temperature. As with uranium, we are unable to state the exact mechanism by which the NdO^+ ions are formed. It seems clear, however, that the two systems are somewhat similar. It is probable that two analogous oxide species are formed on the surface in the two systems. For uranium these two species decompose to give UO^+ and UO_2^+ ions. The analogous neodymium species decompose, both yielding primarily NdO^+ ions.

Comparison of the Nd^+ ion current in Fig. 20 with the U^+ ion current in Fig. 19 is also of interest. The Nd^+ ion current curve contains a low-temperature peak similar to those noted for barium and strontium. While it is impossible to resolve any structure out of these data, it is apparent that there is a low-temperature component to this curve which is in approximate coincidence with the NdO^+ current maximum. Either the species responsible for the low-temperature peak in the NdO^+ curve also decompose to yield Nd^+ ions, or there is another interaction occurring in approximately the same temperature region.

As for uranium, the final answer to these questions must await refinements in the experimental techniques employed.

High-Temperature Region

Figure 21 shows high-temperature Nd^+ ion current data taken in the rapid manner described in the barium-tantalum discussion. Data are included at three different arrival rates. The effect of oxygen on this slope is seen in the lowest arrival rate. In general the effect is negligible at the very highest temperatures. The analysis of 16 runs of this type gives a value of 0.52 ± 0.04 ev for the activation energy, which yields a value of 5.10 ± 0.04 ev for the ionization potential of neodymium.

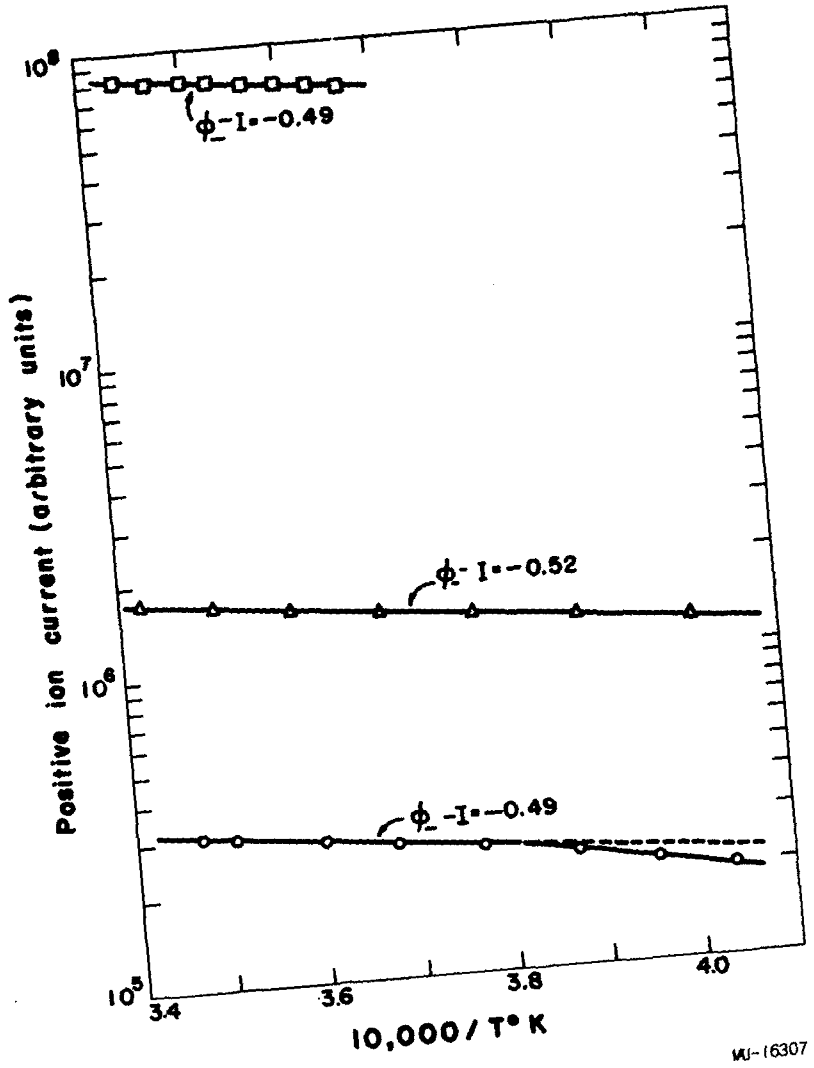


Fig. 21. Ionization of neodymium on tungsten; high-temperature region. Note: Vertical position of curves is arbitrary. Relative position is related to atomic-beam intensity.

It is worth noting that during the course of the neodymium experiments we were able to see the ion current produced by the very small amount of praseodymium impurity in the sample. Although these data were in general rather poor we were able to make two runs which indicated an ionization potential of 5.0 ± 0.1 ev for praseodymium. This value does not agree with the value compiled by Moore[34] (5.76 ev) or with the value of Johnson, Hudson, and Spedding[35] (5.4 ev). These numbers were obtained in manners similar to the values reported by the same authors for neodymium.

It should be noted that the 5.0 ev value which we suggest is subject to considerably more experimental error than are the other results reported in this work. This is because of the relatively poor statistics obtained with the very-low-intensity Pr^+ ion current. It is significant to note that our value for praseodymium is only slightly lower than our value for neodymium. This is also the case in the work of Johnson, Hudson, and Spedding, and it is quite possible that the magnitude of their oxygen interference was approximately the same in both cases. This would lend considerably weight to the validity of the number suggested here.

SUMMARY AND CONCLUSIONS

The Saha-Langmuir equation was verified quantitatively for the ionization of barium on tungsten and for the ionization of barium and strontium on tantalum. The work function obtained in each case was a value consistent with work functions determined by electron-emission experiments. These values based on barium were 4.58 ± 0.02 ev for tungsten and 4.23 ± 0.03 ev for tantalum. The strontium experiment yielded a value of 4.17 ev for the tantalum work function.

Using the Saha-Langmuir theory to describe the ionization of barium and strontium on rhenium yields a rhenium work function of 5.21 ± 0.02 ev based on barium and 5.17 ± 0.02 ev based on strontium. These values are within the limits of the literature values currently available and represent an excellent check of the Saha-Langmuir theory, and fix more accurately the work function of rhenium.

The ionization of uranium on tungsten yields a value of 6.25 ± 0.02 ev for the ionization potential of uranium. This value is based on a tungsten work function of 4.58 ev. This value does not agree with the optical value of 4 ev reported by Keiss, Humphreys, and Lann,[32] nor does it agree with the surface ionization value of about 4.7 ev reported by Rauh.[33]

Ionization of neodymium on tungsten gives a value of 5.10 ± 0.04 ev for the ionization potential of neodymium. This does not agree with the 6.31 ev value reported by Moore[34] nor does it agree with the 5.5 ev reported by Johnson, Hudson, and Spedding.[35]

At temperatures below 2500°K, surface chemical reactions play a large part in the production of positive ion currents. On tungsten surfaces barium interacts with fluorine impurities in the metal to form both Ba^+ and BaF^+ ion currents. Ion-current equilibrium studies following instantaneous temperature changes of the tungsten surface indicate that both these species come to their equilibrium currents at the same rate at very low temperatures. This furnishes quantitative evidence that both peaks are attributable to a fluorine interaction and suggests that the rate of attaining equilibrium represents the rate at which the barium and fluorine concentrations reach a new equilibrium surface concentration following a change in temperature. An interaction between barium and oxygen is indicated at a slightly higher temperature. This interaction is indicated by the apparent composite nature of the low-temperature Ba^+ ion current peak and confirmed by comparison with the uranium and neodymium work on tungsten.

For barium ionizing on tantalum essentially identical results are obtained, except that the interactions due to fluorine and oxygen are both directly identifiable and the two peaks produced are resolved. The lower-temperature fluorine interaction was identified in a manner identical to the above case. The higher-temperature oxygen interaction was identified by the fact that both the Ba^+ and the TaO^+ ion currents equilibrate in the same time following a sudden change in temperature, whereas other impurity ion currents and the Ta^+ ion current equilibrate almost instantaneously.

For barium ionizing on rhenium both BaF^+ and $BaCl^+$ ion currents were identified. In addition, oxygen interactions were indicated, but no BaO^+ or ReO^+ ion currents were detected. No particular effort was made to study the equilibration rates in this case. The extent of these effects is not large for barium on rhenium, primarily because a large fraction of the barium ions is ionized by the Saha-Langmuir process.

The strontium ion current with tantalum was so small that no work could be done at the lower temperatures. For strontium ionizing on rhenium the low-temperature results were qualitatively similar to the barium-rhenium system, although the effects were more pronounced.

No interactions between uranium and fluroine were noted in the uranium-tungsten system. However, at the temperature at which the barium-fluorine interaction was noted on tungsten, essentially no uranium current could be detected, so that even if the predicted uranium-fluorine interaction were taking place we quite possibly could not have seen the ions because of the relatively low volatility of the products.

In contrast to the barium and strontium systems, the behavior of the uranium system was found to be quite strongly dependent on the pressure of the system. The effect could be explained almost entirely by the presence of oxygen. The net effect of oxygen on the system was to drastically decrease the U^+ ion current and to replace it with UO^+ and UO_2^+ ion currents, each peaking at a different temperature. As the amount of oxygen in the system was increased the UO_2^+ ion current increased with respect to the other two ion currents, indicating an equilibrium shift toward the higher oxide. Above temperatures of 2700°K the effect of oxygen on the slope of the Saha-Langmuir line was negligible, indicating that at least one of the atoms involved did not spend sufficient time on the surface to interact.

The low-temperature ionization of neodymium on tungsten was found to be quite similar to the low-temperature uranium-tungsten system. The significant difference is the fact that no NdO_2^+ ion current was observed. However, the NdO^+ ion current curve seems to be a composite curve representing two sources of these ions. Apparently two analogous oxide species are formed in the neodymium and uranium systems. For uranium these two species decompose to give UO^+ and UO_2^+ ions. The analogous neodymium species decompose, both yielding primarily NdO^+ ions. There is evidence indicating that the low-temperature species also yields Nd^+ ions on decomposition.

We may conclude that each system presents its own chemical problems and that a complete understanding of the ionization phenomena on surfaces necessitates the resolution of these chemical reactions. We have not established that the popular concepts of reflection coefficients or work functions changing with very small contaminations are without basis in fact. This work may, however, be interpreted as explaining some of the major effects that have led previous investigators to resort to these explanations. A reflection coefficient simply represents a fraction of the impinging atomic beam that does not take part in the Saha-Langmuir process. In previous investigations of this nature not using mass spectrometric techniques it has been assumed that this represented an actual reflection at the metal surface. Although some reflection of this nature may take place, we find that observable chemical interactions, even on extremely pure metal surfaces, are sufficently probable to account for the observed experimental results. While perhaps applicable in the case of electron emission, charges in bulk surface work functions do not adequately describe our observations. It seems, in fact, rather unrealistic to attempt to describe bulk surface properties on an atomic scale. Romanov and Starodubtsev's studies on the sodium-tungsten system[20] also indicate that this type of treatment is not consistent with observations.

A number of recent papers have discussed the effect of surface nonhomogeneity on positive ion formation. By modifying the Saha-Langmuir equation to account for the difference in work function of the different exposed crystalline planes one can obtain reasonable fits with the data in certain cases. In this procedure one assumes numbers for the fractional coverage of each plane, varying these until agreement is obtained. This is followed by the assumption that the numbers giving agreement with experiment are reasonable values, which--within reasonable limits--is verified by experimental work. Although this effect perhaps exists it can by no means be extended to account for the very high ionization efficiency noted, in say, the barium-tungsten system, nor can it account for the two distinct peaks in the barium-tungsten system. Neither can it account for general differences noted in the shapes of the strontium and barium curves for ionization on rhenium. The failure to see such effects at high temperatures is probably due to low residence time and the apparent absence of migration across grain boundaries.

Although we feel that it is possible, by extensions of the techniques used in this work, to completely resolve and to describe the reactions taking place, it should be noted that the situation is extremely complex. With the barium-tantalum system used as an example, the problem may be outlined in roughly the following manner. For simplification let us assume that for this system the equilibrium barium ion current is a function only of the temperature and the surface concentrations of the atoms that react with barium to form ions. In this case we are concerned primarily with oxygen and fluorine. At a given temperature the amount of fluorine on the surface is governed by the arrival rate at the surface by diffusion from the interior of the metal and by the departure rate from the surface by desorption and reaction with barium. An equilibrium is established, but since the amount of fluorine in the body of the metal is constantly decreasing, this equilibrium is also a slowly varying function of time. In addition, both the arrival rate and departure rate are strong functions of temperature and the rate at which a new equilibrium condition is reached following a change in temperature is rather slow. Exactly the same analysis can be made for atomic oxygen diffusing from the interior of the tantalum. In addition, molecular oxygen is arriving at the surface at a rate governed by the pressure of the system. Since the system warms gradually on starting a run the pressure gradually rises, but fluctuates somewhat since plates near the hot filament are warmed and cooled as the temperature of the hot filament is cycled. In addition there is an equilibrium between molecular and atomic oxygen on the surface, and we have some evidence that both are influential in forming positive ions. Therefore at any given time the concentrations of fluorine and molecular and atomic oxygen on the surface are functions not only of temperature but also of the time that the entire system has been outgassed, of the outgassing history of the filament, and of the immediate temperature of the surroundings. In addition, the effects of oxygen and fluorine overlap, and can be studied separately only at relatively high and relatively low temperatures, regions where the reaction rates are very slow or very fast. Particularly in the region of the fluorine interaction the lifetime of the barium on the surface is quite long and relatively large fractions of the monolayer may build up. When this happens, in addition to adding to the complexity of resolving the effects at this temperature, barium diffuses into the tantalum lattice and forms a resovoir of barium atoms which diffuse out at higher temperatures and add to the arrival rate of barium at the surface. Consequently the behavior of the barium ion current in the region of the oxygen interaction depends temporarily on whether the temperature was increased or decreased in arriving at the region of interest. Also in each case an appreciable Ba^+ background current was noted from the metal itself, but this became negligible after a reasonable aging period.

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