

Formation of Positive and Negative Ions on Rhenium, Oxygenated Tungsten, Hafnium, Lanthanum Hexaboride, and Thoriated Tungsten Surfaces*

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Yields are reported for the formation of positive and negative ions from molecular beams striking various surfaces. Negative ions are formed from beams of several halogen compounds and tetracyanoethylene on Re, Hf, thoriated W, and LaB₆ with efficiencies ranging up to a maximum of 2.6×10^{-2} for KCl on thoriated W (activated). This filament may be useful in detectors for some molecular-beam studies. The efficiencies for the formation of positive ions from K and potassium halides are generally in agreement with the Sahal-Langmuir model. They are near unity on oxygenated W, Re, and thoriated W (deactivated by heating to deplete the thorium) but much lower (2.5 – 6.6×10^{-3}) on thoriated tungsten (activated).

I. INTRODUCTION

Molecular beams of chemical species with low ionization potentials, such as alkali atoms, are usually detected by recording the current of ions formed when these species hit a hot metal surface, such as tungsten or platinum, which has a high work function. This method is extremely sensitive to the species making up the beam, having a detection efficiency of nearly unity for K atoms on tungsten and platinum surfaces (Ref. 1, for example). A second advantage is that other molecules, such as O₂ and H₂O, commonly present in vacuum systems, produce a negligible amount of ionization because of their higher ionization potentials. Several reviews² describe the theoretical and experimental research on this process which is called positive surface ionization. The ionization of alkali atoms and alkali halides on tungsten surfaces was extensively investigated by Phipps, Copley, and co-workers³ and by Datz and Taylor⁴ who also studied ionization on platinum surfaces. Wilson and Ivanetich⁵ investigated the ionization of LiI, Na, Rb, and NaI on tungsten, rhenium, and platinum surfaces. The ionization efficiencies reported in Refs. 3–5 are relative to efficiencies of ionization on oxygenated tungsten surfaces which are assumed to be 1.0 for alkali atoms and alkali halides.

Up to the present the chemical applications of molecular beams have been restricted almost com-

pletely, in practice, to a small class of reactions because of the important advantages of these surface ionization detectors. Many people have realized that a similar process, in which negative ions are formed from molecules containing fragments of high electron affinities (such as halogen atoms) on low work-function surfaces, might be a promising way to extend molecular-beam experiments to a wider range of reactions.

Here we report on a study of negative surface ionization for one cyano and several halogen compounds in beams hitting one of several different filaments. Comparison with a simple model for effusion and with positive ionization of several molecules on other surfaces gives a quantitative indication of ionization efficiencies. The efficiencies on thoriated tungsten are in the range 3.0×10^{-5} – 2.6×10^{-2} . Although these are small compared to the yields for positive ions on surfaces with high work functions, they may be sufficient to make negative-ionization detectors useful for some beam experiments.

II. APPARATUS AND EXPERIMENTAL PROCEDURE

A. General Description

The measurements were carried out in a vacuum of 3 – 10×10^{-7} torr, produced by a commercial test stand. A vertical cut through the center of the apparatus is shown in Fig. 1(a). The essential parts are a rotatable molecular-beam source (S), a hot filament (F) on which the beam particles are ionized, an electrode (C) to collect the ions, a magnetic field (B) parallel to the filament to reduce the electron current to the collector, and a brass shield (SH), cooled with liquid nitrogen, around the collector to reduce the pressure of condensable vapors near the filament. In addition, a movable shutter [not shown in Fig. 1(a)] can keep the beam from reaching the detector.

The filament is spot welded to two stainless-steel supports (SU), one of which is fitted with a spring to keep tension on the filament. The collector is a stainless-steel ring (15 mm high, 36 mm in diam,

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§ Contribution No. 3619.

¹ W. Schroen, *Z. Physik* **176**, 237 (1963).

² For example: (a) E. Ya. Zandberg and N. I. Ionov, *Usp. Fiz. Nauk* **57**, 581 (1959) [*Sov. Phys.—Usp.* **2**, 255 (1959)]; (b) M. Kaminsky, *Atomic and Ionic Impact Phenomena on Metal Surfaces* (Academic Press Inc., New York, 1965), pp. 98–142.

³ (a) M. J. Copley and T. E. Phipps, *Phys. Rev.* **45**, 344 (1934); (b) M. J. Copley and T. E. Phipps, *ibid.* **48**, 960 (1935); (c) J. O. Hendricks, T. E. Phipps, and M. J. Copley, *J. Chem. Phys.* **5**, 868 (1937); (d) A. A. Johnson and T. E. Phipps, *ibid.* **7**, 1039 (1939).

⁴ S. Datz and E. H. Taylor, *J. Chem. Phys.* **25**, 389, 395 (1956).

⁵ K. R. Wilson and R. J. Ivanetich, University of California, Lawrence Radiation Lab. Rept. UCRL-11606, 1964.

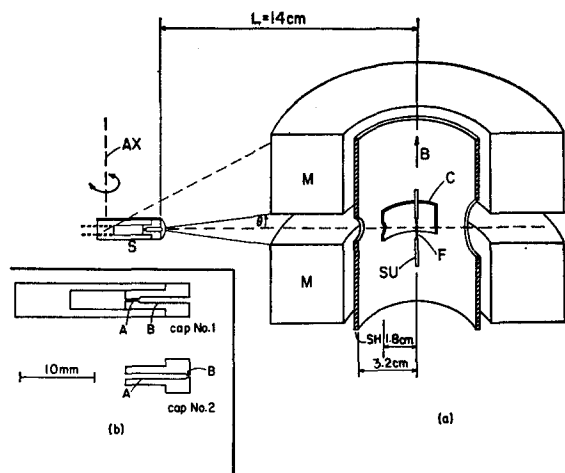


FIG. 1. Schematic diagram of apparatus for studying surface ionization (a) section through center: S—beam source, AX—pivot axis for beam source, SH—cold shield, F—filament, SU—support for filament, C—collector, M—magnetic coil, B—direction of magnetic field. (b) Source used for solid materials having vapor pressures below 10^{-2} torr at room temperature and the caps used for this source: cap No. 1 is shown in place and cap No. 2 is shown separately below it. A and B label the segments of the channels in the caps.

and 1 mm thick), with the part away from the beam source (about 40% of the ring) cut away. The beam enters the detector through holes in the cold shield and in the collector and leaves through a second hole in the cold shield. The diameter of the hole in the collector is 7.0 mm. The collector current is read on a vibrating-reed amplifier (Applied Physics Corporation Model 30).

B. Beam Sources

One of the two stainless-steel sources is shown in Fig. 1(b). This source is used for solid materials that have vapor pressures below 10^{-2} torr at room temperature. The beam material is placed inside this source and effuses through a hole in its cap. The two caps that are used with this source are also shown. Cap No. 1 was used for all the surface ionization measurements reported here. Cap No. 2 was used for comparing experimental effusion fluxes with theoretical values as explained in Sec. III. As shown in the figure, the channel in each of the two caps consists of two segments having different diameters. These

TABLE I. Dimensions (millimeter) of channels in the caps of the beam sources.^a

	Cap No. 1	Cap No. 2
d_A	0.250	0.625
l_A	1.85	8.7
d_B	0.675	0.238
l_B	7.0	0.17 ± 0.01

^a d_i is the diameter and l_i the length of segment i . See Fig. 1(b).

segments are labeled A and B. The diameters d_A and d_B and lengths l_A and l_B are given in Table I, where the accuracy is about $\pm 2\%$ unless otherwise indicated. The source is placed in an electrically heated ceramic tube (not shown in Fig. 1). The temperature of the source is measured with a calibrated thermocouple (chromel–alumel or copper–constantan).

The source used for compounds with vapor pressures greater than 10^{-2} torr at room temperature is identical to the first one, except that in this case the reservoir is outside the vacuum system in a tube cooled in a bath. The connection from the reservoir to the part of the source inside the vacuum chamber is by a piece of flexible stainless-steel tubing (20 cm long, 1 mm i.d.). The temperature of the cold bath is measured with a calibrated iron–constantan thermocouple.

The part of the source from which the beam effuses is mounted on a rotatable rod so that the beam can be directed toward or away from the filament.

C. Magnetron

The magnetic field is produced by a current flowing in two coils of copper wire. A field up to 150 G can be obtained with these coils. Hull gives^{6,7} an expression,

$$B_{\text{cutoff}} = \frac{(8EM/e)^{1/2}}{r_c[1 - (r_f/r_c)^2]}, \quad (1)$$

for the magnetic field which is needed to cut off the current of particles with mass M and charge e coming with a negligible initial velocity from a cylindrical filament and flowing to a coaxial cylindrical collector. E is the attractive voltage between the filament and collector and r_f and r_c are the radii of the filament and the collector, respectively.

For the experimental conditions of this work ($E \approx 4$ V, $r_c = 1.8$ cm, and $r_f \ll r_c$) the calculated value of the magnetic field needed to cut off the electron current to the collector is 7.4 G. The actual extent of reduction in the electron current is found to depend on the pressure in the system. Typical results are those described in Fig. 2 for a thoriated-tungsten filament (0.15 mm diam and 10 mm long) at 1800°K in the absence of any beam. In the presence of a beam the background of electrons is found to go up as the intensity of the beam is increased. Background currents up to about 10^{-10} A are sometimes measured for the most intense beams. The currents of negative ions in this study are in the range 10^{-13} – 10^{-9} A. These are usually bigger by a factor of 2–20 than the background of electrons under the same conditions.

D. Filaments

The diameters or widths of the filaments that are described here are accurate to about $\pm 3\%$.

⁶ A. W. Hull, Phys. Rev. **18**, 31 (1921).

⁷ L. Brillouin, Phys. Rev. **60**, 385 (1941).

1. Hafnium and Rhenium

The hafnium and rhenium used are commercial samples (both from United Mineral and Chemical Corp., N.Y.), without any further treatment except for aging in good vacuum at a high temperature ($\sim 1800^\circ$ and 2700°K , respectively) for several minutes. The rhenium filament is a wire 12 mm long, 0.125 mm diam. The hafnium filament is made of a strip of Hf (0.40 mm wide \times 0.04 mm thick \times 10 mm long) spot welded to a rhenium support (0.125 mm diam and 12 mm long).

2. Thoriated Tungsten

a. Carbonization: A standard procedure for producing stable electron emission at a high current level from thoriated-tungsten filaments is carbonization by heating in a hydrocarbon atmosphere (Ref. 8, pp. 280–290). In the present work carbonization is necessary for getting the highest efficiencies for negative surface ionization. The efficiency of ionization of carbon tetrabromide on an uncarbonized thoriated-tungsten filament is found to be about one hundred times lower than it is on a carbonized filament.

The conditions that we find to be most effective for carbonization are maintaining the filament at 2350°K for 15–30 min, at a hydrocarbon pressure of about 5×10^{-6} torr. As a source of hydrocarbon we use the oil vapor from the diffusion pump of the

vacuum system. An appropriate amount of this vapor enters the vacuum chamber when the main trap is not cooled by liquid nitrogen. Attempts to improve the operation of the filament further, by additional carbonization with other hydrocarbons under different conditions, were unsuccessful.

The reproducibility of the method of carbonization was checked by carbonizing two filaments having different dimensions (a wire 0.15 mm diam and 11 mm long, and a ribbon 0.75 mm wide \times 0.025 mm thick \times 11 mm long from H. Cross Co., N.J., containing 0.75% Th), and measuring the ionization efficiency of CBr_4 on each. The efficiencies found for the two carbonized filaments are equal within a factor of 1.2. Most of the measurements on thoriated tungsten were carried out with the 0.15-mm-diam wire.

b. Activation: In order to maintain a layer of thorium on the surface of the carbonized thoriated tungsten filament, the latter is heated occasionally for 1 or 2 min to about 2200°K .

3. Oxygenated Tungsten

The oxygenated tungsten filament was prepared by aging a tungsten wire (0.094 mm diam and 11 mm long from Callite Tungsten Corp., Union City, N.J.), at 1500°K for 3 min in the presence of air at a pressure of 10^{-4} torr.

4. LaB_6 Coated on Rhenium Wire

We used two methods recommended in the literature for coating a rhenium filament with a layer of LaB_6 .

(a) A mixture of LaB_6 , Duco cement, and butyl acetate is painted on the rhenium wire (0.15 mm diam and 11 mm long) and dried by passing a current through it.^{9,10}

(b) The rhenium wire is coated with LaB_6 by a cathodoresis process in a suspension of LaB_6 in methanol.^{11,12}

The second method gives a better coating than the first, but in both cases the LaB_6 flakes off the filament easily. The use of a purer sample of LaB_6 is recommended¹³ for making a stronger bond to the support.

E. Measurements of Electronic Work Functions

We find the electronic work function of a filament (ϕ_e) from the experimental measurements by applying the Richardson equation

$$J = AT^2 \exp(-\phi_e/kT), \quad (2)$$

⁹ W. D. Dong, W. D. Kilpatrick, J. M. Teem, and D. E. Zuccaro, *Progr. Astron. Aeron.* **9**, 269 (1963).

¹⁰ J. M. Lafferty, *J. Appl. Phys.* **22**, 299 (1951).

¹¹ L. J. Favreau, *Rev. Sci. Instr.* **36**, 856 (1965).

¹² J. D. Buckingham, *Brit. J. Appl. Phys.* **16**, 1821 (1965).

¹³ L. J. Favreau and D. F. Koenig, *Rev. Sci. Instr.* **38**, 841 (1967).

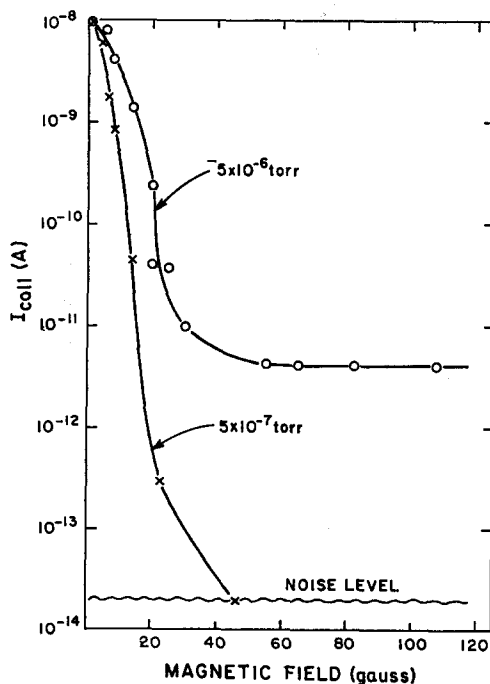


FIG. 2. Dependence of collector currents, for electrons emitted from a thoriated-tungsten filament at 1800°K , on the magnetic field parallel to the filament, for two pressures in the system.

⁸ W. H. Kohl, *Materials and Technique for Electron Tubes* (Reinhold Publ. Corp., New York, 1960).

TABLE II. Emissivity data and experimental electronic work functions for various filaments.

Filament	$\epsilon_{0.65}$ at 2000°K	ϕ_e (eV)
Re	0.42	5.0±0.1
Hf	0.445	3.75±0.1
LaB ₆	0.42	3.3±0.15
W(Th)	0.435	2.8±0.1
W(Th) ^a	0.435	4.6±0.1

^a Thoriated tungsten with thorium depleted by heating to ~2600°K for several hours.

where J is the saturation electron-current density, emitted from the surface at an absolute temperature T , A is a constant, and k is Boltzmann's constant.

We measure the apparent filament temperatures (T_i) with an optical pyrometer (The Pyrometer Instrument Co., Bergenfield, N.J., Model 95, with guaranteed accuracy between $\pm 4^\circ$ at 1000°K and $\pm 10^\circ$ at 2800°K), and then find the true temperatures (T), by using the equation^{14,15}

$$T^{-1} - T_i^{-1} = \frac{0.65}{1.4388 \times 10^4} \ln[\epsilon_{0.65} \times 0.900], \quad (3)$$

where $\epsilon_{0.65}$ is the emissivity of the filament at a wavelength of 6500 Å and temperature T , 0.900 is the value used for the transmission of the glass,¹⁵ through which we observe the filament, and the temperatures are given in degrees Kelvin. Values for $\epsilon_{0.65}$ for different filaments are taken from Ref. 8 (Re, p. 528; Hf, p. 534; and W, p. 621). We found no data in the literature for the emissivity of LaB₆ and arbitrarily use a value equal to that of Re. Table II summarizes the emissivity values at 2000°K and the electronic work functions found by using Eq. (2). The electronic work functions listed are average values from several measurements carried out during the period that each of the filaments was tested for surface ionization.

F. Procedure for Ionization Measurements

All the experiments were carried out with a constant geometry of the system. This permits a comparison of the efficiencies with which various molecules are ionized on a set of different filaments. The measurements recorded are the differences in ion currents when the beam is directed toward or away from the filament. For every compound on a given filament the collected signal was measured over a range of pressures (usually between 10^{-4} and 10^{-1} torr) inside the source. Measurements were carried out

¹⁴ C. M. Herzfeld, *Temperature, Its Measurement and Control in Science and Industry* (Reinhold Publ. Corp., New York, 1962), Vol. 3, Pt. 1, p. 539.

¹⁵ P. D. Foote, C. O. Fairchild, and T. R. Harrison, Natl. Bur. Std. (U.S.) Technol. Papers No. 170 (1921).

with a magnetic field of about 150 G. The filament was held at -4 V with respect to the collector (at ground potential) for the collection of negative ions and at $+4$ V for positive ions.

Ionization efficiencies are calculated from the experimental measurements as explained in Sec. III.

G. Vapor-Pressure Data

The sources of vapor-pressure data used in this work are listed in Table III. For most of these compounds vapor pressures below 1 torr are obtained by extrapolation of the $\log P$ vs $1/T$ plots with correction, where necessary, for any phase change using heats of these changes given in Ref. 16.

III. RESULTS

As an aid in describing our results we consider first an extremely simple model for surface ionization.² We imagine that the molecules of a beam which hit a surface are adsorbed and dissociated, part of the fragments are ionized, and a thermodynamic equilibrium is established between the neutral fragments, ions, and electrons on the surface. For the purpose of illustration we choose the case of an alkali halide (MX) beam that can be ionized either posi-

TABLE III. Sources of vapor-pressure data.

Compound	Ref.
KCl and (KCl) ₂	a
KBr and (KBr) ₂	a
KI and (KI) ₂	a
K	a, b
CCl ₄	c
C ₂ Cl ₆ (hexachloroethane)	c
C ₆ H ₅ Cl (chlorobenzene)	c
C ₆ H ₅ Br (bromobenzene)	c
C ₆ H ₅ I (iodobenzene)	c
C ₂ H ₅ I (ethyl iodide)	c
Br ₂	d
I ₂	d
CBr ₄	e
HI	f
TCNE (tetracyanoethylene)	g

^a Calculations from thermodynamic data of *JANAF Tables* (1965).

^b U. Buck and H. Pauly, *Z. Physik. Chem.* **44**, 345 (1965).

^c T. E. Jordan, *Vapor Pressures of Organic Compounds* (Interscience Publishers, Inc., New York, 1954).

^d R. E. Honig and H. O. Hook, *RCA Rev.* **21**, 360 (1960).

^e R. S. Bradley and T. Drury, *Trans. Faraday Soc.* **55**, 1844 (1959).

^f *Handbook of Chemistry and Physics*, R. C. Weast, Ed. (Chemical Rubber Company, Cleveland, Ohio, 1966), 47th ed.

^g R. H. Boyd, *J. Chem. Phys.* **38**, 2529 (1963).

¹⁶ *Landolt-Börnstein, Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1961), Vol. 2, Pt. 4.

tively or negatively. The relative amounts of neutrals and ionized species evaporating from the surface, under steady-state conditions, are given for this method by the Saha-Langmuir equation, for positive ionization

$$n_{M^+}/n_M = (g_{M^+}/g_M) \exp[(\phi - I)/kT] \quad (4)$$

and for negative ionization

$$n_{X^-}/n_X = (g_{X^-}/g_X) \exp[(E.A. - \phi)/kT]. \quad (5)$$

Here n_i is the number of species i leaving the surface in unit time, g_i is the statistical weight of species i , and the subscripts M^+ , X^- , M , and X refer to positive alkali metal ions, negative halide ions, alkali-metal atoms, and halogen atoms, respectively. In the same order the values for g_i are very nearly equal to 1, 1, 2 and $[4 + 2 \exp(-\Delta E/kT)]$, where ΔE is the energy difference between the $^2P_{3/2}$ ground state and the $^2P_{1/2}$ excited state of X ($\Delta E_{Cl} = 0.109$ eV, $\Delta E_{Br} = 0.457$ eV, and $\Delta E_I = 0.943$ eV¹⁷). The relative contribution of the $^2P_{1/2}$ excited state is small at temperatures near 2000°K (about 20% for chlorine and much less for bromine and iodine). I is the ionization potential of the alkali atom, $E.A.$ is the electron affinity of the halogen atom, and ϕ is the work function of the hot surface. In this model we ignore the nonuniformity of the surface, any reflection of particles from the surface, any lack of equilibrium on the surface, interactions between atoms on the surface or with the surface, and the contribution of more than one species to the total current. We assume that ions of one charge are held on the filament, by the potential of the filament with respect to the collector, when ions of opposite charge are being collected.

The quantities that are measured experimentally are currents of ions leaving the hot filament for given beam conditions. In order to compare the experimental results with those predicted from Eqs. (4) or (5), we need to know the number of neutral atoms leaving the surface n_M or n_X . This should be measured or calculated from

$$N = n_{M^+} + n_M \quad (6a)$$

or

$$N = n_{X^-} + n_X, \quad (6b)$$

where N is the number of beam particles incident on the filament in unit time. Knowing N we can find the ionization efficiency which we define by

$$\beta_{\pm} = n_{\pm}/N. \quad (7)$$

We estimate β in two ways. In the first we find the number of molecules N of an ideal gas which hit an area A_{fil} of the filament, after effusing from a small hole of area A_{source} in a source chamber at a distance L away from the filament. First we obtain

the expression for N when cap No. 2 is used in our source because the length/diam (l/d) ratio of the channel segment with the smaller diameter (B) is similar to that for which Clausing^{18,19} made angular distribution calculations ($l/d=1$). We assume that the effusion characteristics are determined, for cap. No. 2, mainly by the segment with the smaller diameter. For molecular flow conditions, the number of molecules escaping in unit time from a source, through a short cylindrical channel, into a cone of solid angle $\Delta\omega$ centered at an angle θ from the oven normal (see Fig. 1) is given by

$$N(\theta) = [\rho \bar{v} A_{source} D(\theta)/4\pi] \cos\theta \Delta\omega \\ = [N_A P A_{source} D(\theta)/(2\pi R m T)^{1/2} \pi] \cos\theta \Delta\omega. \quad (8)$$

ρ is the number density and \bar{v} the average velocity of molecules of molecular weight m in the source at an absolute temperature T and pressure P . R is the gas constant, N_A is Avogadro's number and $D(\theta)$ is a numerical factor which decreases as θ increases. For channels with $l=d$, $D(0^\circ) \cos 0^\circ$ is 1.0 and $D(10^\circ) \cos 10^\circ$ is 0.88.

The dimensions of the filaments in our experiments are small compared to the distance to the source (L). Therefore we may assume to a good approximation that the filament is located at $\theta=0^\circ$ when the maximum signal is observed, and the solid angle intercepted by the filament is A_{fil}/L^2 . Then from Eq. (8) we have

$$N = [N_A P A_{source}/(2\pi R m T)^{1/2}] (A_{fil}/\pi L^2). \quad (9)$$

The efficiency of ionization is thus given by

$$\beta_{\pm} = \Delta I_{\pm} N_A / F_{\epsilon_{011}} N = K \cdot S_{\pm}, \quad (10)$$

where we have used the definitions

$$K = (2\pi R)^{1/2} \pi L^2 / F_{\epsilon_{011}} A_{source} \quad (11)$$

and

$$S_{\pm} = \Delta I_{\pm} (T m)^{1/2} / A_{fil} P. \quad (12)$$

ΔI_{\pm} is the difference between the ion currents (positive or negative) when the beam is directed toward or away from the filament, F is the Faraday, and ϵ_{011} is the fraction of ions formed at the filament that reach the collector. We estimate ϵ_{011} to be approximately 0.90 because experiments in which potassium halides are positively ionized on rhenium show that an increase in the filament to collector-voltage difference from +4 V to +10 V causes an increase in the collector current by about 10%, but further increase of the voltage to +22 V does not have any effect on the collector current. K is a constant determined by geometrical factors. S contains the variable parameters in our system as well as the col-

¹⁷ C. E. Moore, Natl. Bur. Std. (U.S.) Circ. No. 467, 1 (1949), 2 (1952) 3 (1958).

¹⁸ P. Clausing, Z. Physik **66**, 471 (1930).

¹⁹ L. B. Loeb, *The Kinetic Theory of Gases* (Dover Publications Inc., New York, 1961), 3rd ed., pp. 301-310.

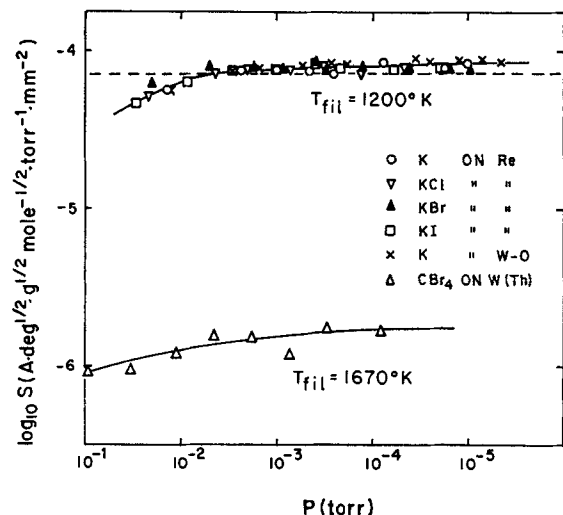


FIG. 3. Dependence of reduced ionization currents S on the pressure in the beam source for the positive ionization of K on oxygenated tungsten, K, KCl, KBr, and KI on rhenium, and the negative ionization of CBr_4 on thoriated tungsten. The temperatures indicated are those for maximum yields. The horizontal dashed line represents the value of S calculated from consideration of the effusion rates assuming an ionization efficiency $\beta=1.0$ (see text).

lector current. We record this reduced quantity in comparing results for different beams and filaments.

For the conditions of our experiments the calculated value of K for cap No. 2 is (expressed in the same units as S),

$$K_2 = 2.7 \times 10^4 \text{ A}^{-1} \cdot \text{deg}^{-1/2} (\text{mole/g})^{1/2} \text{ torr} \cdot \text{mm}^2.$$

We require the value of K for cap No. 1 (K_1), because all the ionization measurements that we report here were done with this cap. We evaluate K_1 experimentally by comparing the values of S_1 and S_2 , using cap No. 1 and cap No. 2, respectively, for the ionization of potassium on a rhenium filament. The ratio S_1/S_2 found over the range of oven pressures 10^{-6} – 10^{-2} torr is 1.9 ± 0.1 . Thus the theoretical value of S_1 for 100% efficiency ($\beta=1.0$), is obtained from Eq. (10),

$$\begin{aligned} S_1(\beta=1.0) &= 1.0/K_1 \\ &= S_1/K_2 S_2 \\ &= 7.2 \times 10^{-5} \text{ A} \cdot \text{deg}^{1/2} (\text{g/mole})^{1/2} \text{ torr}^{-1} \cdot \text{mm}^{-2}. \end{aligned}$$

This value of S is indicated by a horizontal dashed line in Figs. 3 and 4 and is very close to the experimental value for potassium ionized on rhenium and on oxygenated tungsten for an oven pressure of 10^{-3} torr.

In the second way of estimating β we assume that the ionization efficiency is unity for potassium atoms on rhenium (or oxygenated tungsten) as P approaches zero. The efficiency of ionization of particle B on

filament F is then given by

$$\begin{aligned} \beta_{B \text{ on } F} &= (S_{B \text{ on } F}/S_{K \text{ on } Re}) \beta_{K \text{ on } Re} \\ &= (S_{B \text{ on } F}/S_{K \text{ on } Re}) 1.0, \end{aligned} \quad (13)$$

where the S values are calculated from Eq. (12).

The experimental results are shown in Figs. 3–11 and summarized in Table IV. Figure 3 shows the variation of S with source pressure P for the formation of positive ions from K on oxygenated tungsten and K, KCl, KBr, and KI on rhenium, and negative ions from CBr_4 on thoriated tungsten, in each case for the filament temperature that gives the largest yield of ions ($T_{fil}=1200^\circ\text{K}$ for the positive ionization and $T_{fil}=1670^\circ\text{K}$ for the negative ionization). The agreement between the five different measurements of positive ionization shown in Fig. 3 is good. The drop in S for the higher range of P is characteristic of all the cases that we report, except for C_6H_5Cl and C_6H_5Br on thoriated tungsten where there is a rise at the higher pressures.

Figures 4–11 show the dependence of the ionization yields on the temperature of the filament ($\log S$ vs $1/T$). In all cases we have interpolated or extrapolated to a source pressure of 10^{-3} torr.

Figure 4 shows S for positive ions formed from K on

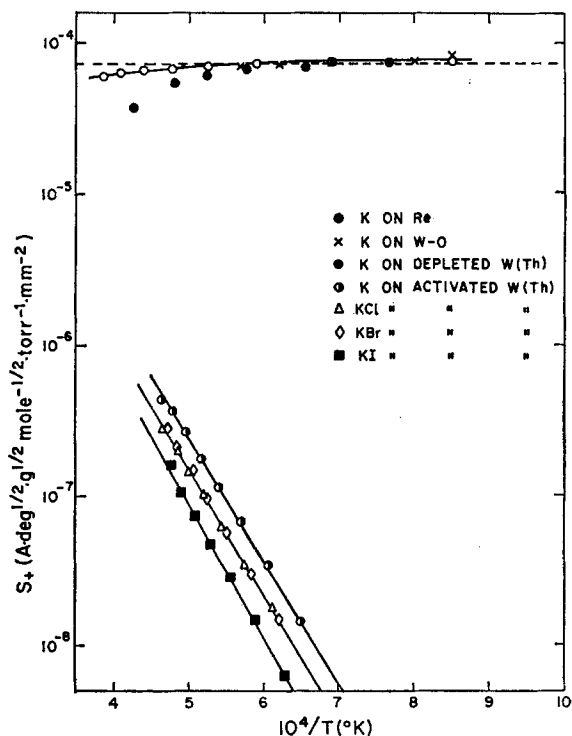


FIG. 4. Reduced ionization currents S_+ of positive ions vs $1/T$, for K atoms incident on rhenium, oxygenated tungsten, and depleted thoriated tungsten, and for K, KCl, KBr, and KI on activated thoriated tungsten for a source pressure $P=10^{-3}$ torr. The horizontal dashed line represents the value of S_+ calculated from effusion-rate considerations assuming an ionization efficiency $\beta=1.0$.

TABLE IV. Ionization efficiencies β for molecules on various filaments relative to that of K on Re at $^{*}1200^{\circ}\text{K}$.

Filament	Beam molecule	Charge of ions collected	β		Maximum efficiency	
			1600°K	1800°K	$T_{\text{fil}}(^{\circ}\text{K})$	β_{max}
Re	K	+	0.96	0.93	1200	1.0
W-O	K	+	0.96	0.93	1200	1.0
Re	KCl ^b	+	0.98	0.96	1200	1.0
		-	...	2.9×10^{-4}	2000	8.7×10^{-3}
	KBr ^b	+	0.98	0.95	1200	1.0
		-	$<3 \times 10^{-5}$	$<3 \times 10^{-5}$
	KI ^b	+	0.98	0.95	1200	1.0
		-	$<3 \times 10^{-5}$	$<3 \times 10^{-5}$
TCNE	-	...	$<10^{-5}$	2440	1.4×10^{-3}	
W(Th)	K	+	3.0×10^{-4}	1.1×10^{-3}	2160 ^c	6.6×10^{-3}
W(Th) ^a		+	0.91	0.86	1300	0.96
W(Th)	KCl ^b	+	1.8×10^{-4}	6.8×10^{-4}	2160 ^c	4.2×10^{-3}
		-	...	5.0×10^{-3}	1620	2.6×10^{-3}
	KBr ^b	+	1.8×10^{-4}	6.8×10^{-4}	2160 ^c	4.2×10^{-3}
		-	...	2.8×10^{-3}	1620	1.3×10^{-3}
	KI ^b	+	0.88×10^{-4}	3.7×10^{-4}	2160 ^c	2.5×10^{-3}
		-	...	3.0×10^{-4}	1600	1.8×10^{-3}
	CCl ₄	-	...	1.2×10^{-3}	1740	1.5×10^{-2}
	C ₂ Cl ₆	-	...	1.3×10^{-3}	1750	1.4×10^{-2}
	C ₆ H ₅ Cl	-	...	1.7×10^{-3}	1700	2.6×10^{-3}
	Br ₂	-	...	2.5×10^{-3}	1670	4.5×10^{-3}
	CBr ₄	-	...	6.6×10^{-3}	1640	1.9×10^{-2}
	C ₆ H ₅ Br	-	...	5.7×10^{-4}	1620	1.4×10^{-3}
	I ₂	-	6.3×10^{-3}	3.1×10^{-3}	1600	6.3×10^{-3}
	HI	-	...	1.8×10^{-4}	1800	1.8×10^{-4}
	C ₂ H ₅ I	-	7.3×10^{-4}	3.7×10^{-4}	1640	7.7×10^{-4}
	C ₆ H ₅ I	-	1.4×10^{-3}	5.3×10^{-4}	1640	1.5×10^{-3}
	TCNE	-	...	2.0×10^{-3}	2080	3.9×10^{-3}
Hf	CCl ₄	-	...	7.3×10^{-4}	1770	7.7×10^{-4}
		-	1.5×10^{-4}	1.4×10^{-4}	1700	2.4×10^{-4}
	Br ₂	-	...	3.6×10^{-4}	1730	4.5×10^{-4}
	CBr ₄	-	2.5×10^{-4}	2.8×10^{-4}	1730	3.2×10^{-4}
	I ₂	-	7.9×10^{-5}	4.4×10^{-5}	1630	8.4×10^{-5}
	C ₆ H ₅ I	-	...	3.0×10^{-5}	1800	3.0×10^{-5}
	TCNE	-	...	2.1×10^{-4}	1800	2.1×10^{-4}
LaB ₆	CCl ₄	-	1.1×10^{-2}	...	1600	1.1×10^{-2}
		-	1.2×10^{-2}	...	1540	1.4×10^{-2}
	C ₆ H ₅ I	-	2.5×10^{-3}	...	1540	3.1×10^{-3}

^a W(Th) with Th depleted by heating to $\sim 2600^{\circ}\text{K}$ for several hours.^b Dimers (taken as at their equilibrium concentration at the oven

temperature) assumed to yield two ions.

^c Maximum temperature used to avoid deactivation of the filament.

rhodium, oxygenated tungsten, and thoriated tungsten. The thoriated tungsten was used both activated to produce a low work-function surface and after the Th was depleted to raise the work function. Also shown are values of S for positive ions formed from KCl, KBr, and KI on activated thoriated tungsten. The slopes are negative for the low work-function surface and positive for the high work-function surfaces (rhodium, oxygenated tungsten, and depleted thoriated tungsten). The values of S for the ionization of K on the three high work-function surfaces

are the same, within the experimental error, for low filament temperatures. The results for positive ionization of KCl, KBr, and KI on rhodium are almost the same as those found for K on rhodium. They are omitted from Fig. 4 in order to avoid crowding.

Figure 5 shows S for negative ions formed from KCl, KBr, and KI on an activated thoriated-tungsten filament, and for KCl on rhodium. The slopes for the thoriated-tungsten filament are positive. The maximum S is of the same order as it is for positive ions formed on the same surface, and much lower

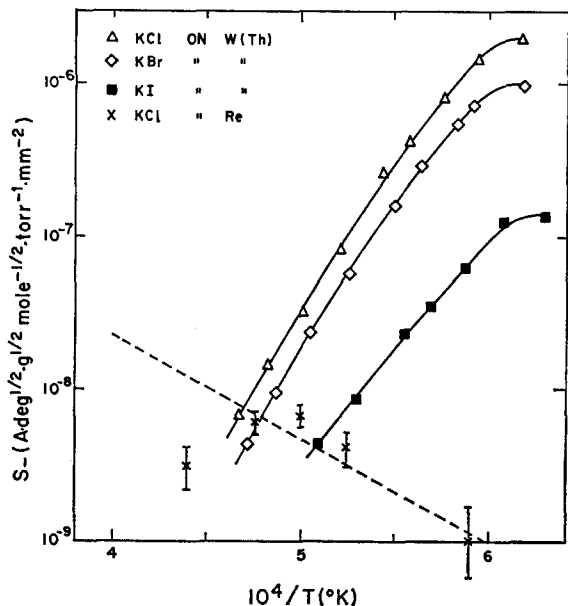


FIG. 5. Reduced ionization currents S_- of negative ions vs $1/T$ for the ionization of KCl, KBr, and KI on activated thoriated tungsten and for KCl on rhenium for a source pressure $P=10^{-3}$ torr. The dashed line represents the predicted values for KCl on rhenium, calculated from Eq. (5).

than for positive ions formed on high work-function surfaces. The efficiency for the negative ionization of KCl on rhenium is very low and small currents ($0.1-0.6 \times 10^{-12}$ A) are observed only at relatively high oven pressures ($\sim 3 \times 10^{-2}$ torr). Extrapolations of S values to 10^{-3} torr are done using the pressure dependence of S for positive ionization shown in Fig. 3. Because of the small values of collector currents the experimental errors are relatively big as indicated in Fig. 5. The dashed line in Fig. 5 represents the theo-

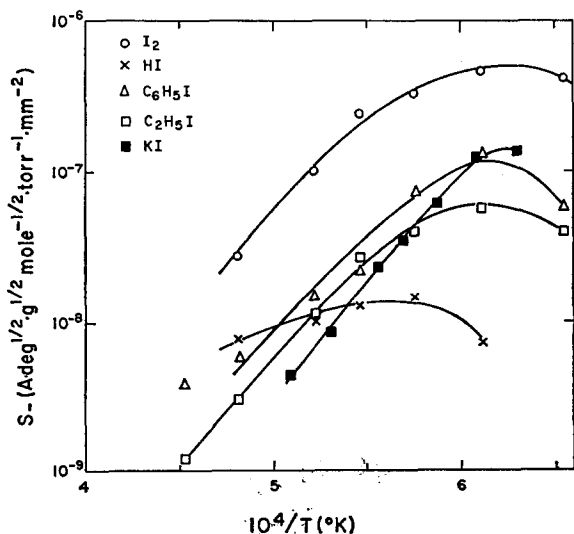


FIG. 6. Reduced ionization currents S_- of negative ions vs $1/T$ for several iodine compounds incident on an activated thoriated-tungsten filament for a source pressure $P=10^{-3}$ torr.

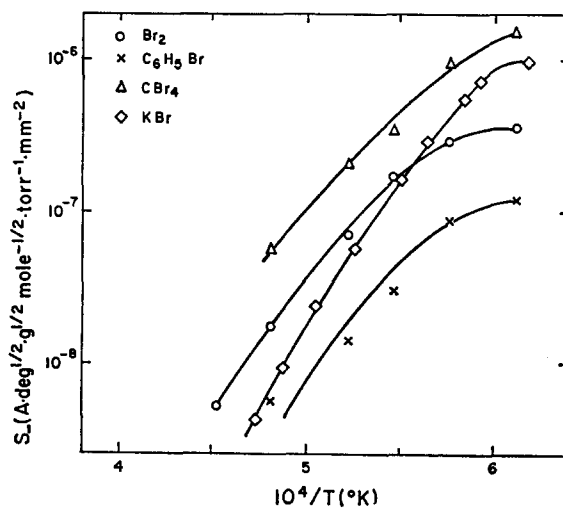


FIG. 7. Reduced ionization currents S_- of negative ions vs $1/T$ for several bromine compounds incident on an activated thoriated-tungsten filament for a source pressure $P=10^{-3}$ torr.

retical values of S as calculated by Eq. (5) for $\phi_{\text{Re}}=5.0$ eV and $E.A._{\text{Cl}}=3.61$ eV.²⁰

No collector currents, within the detection limit of our apparatus (0.1×10^{-12} A), are observed for the negative ionization of KBr and KI on rhenium, up to source pressures of 3×10^{-2} torr. This fact enables us to calculate only the upper limits of the ionization efficiencies for these two molecules on rhenium, as given in Table IV.

Figures 6-8 show similar plots for negative ionization for several iodine, bromine, and chlorine compounds on an activated thoriated tungsten filament. The slopes are positive except at the lowest tem-

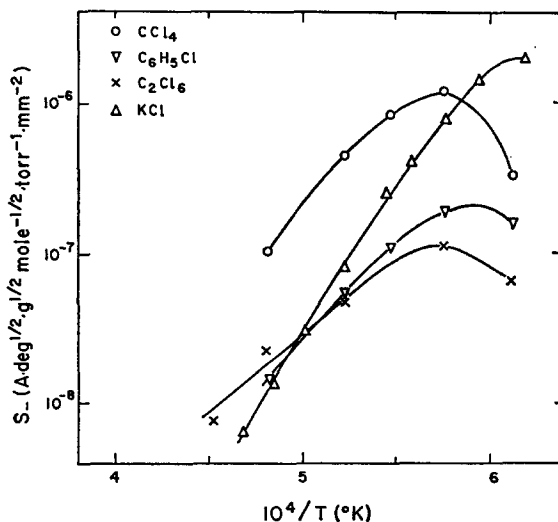


FIG. 8. Reduced ionization currents S_- of negative ions vs $1/T$ for several chlorine compounds incident on an activated thoriated-tungsten filament for a source pressure $P=10^{-3}$ torr.

²⁰ R. S. Berry and C. W. Reimann, *J. Chem. Phys.* **38**, 1540 (1963).

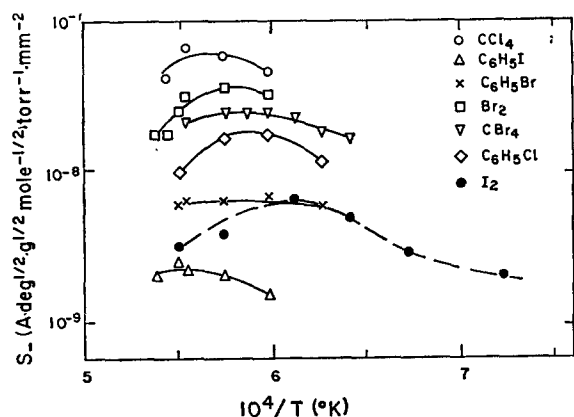


FIG. 9. Reduced ionization currents S_- of negative ions vs $1/T$ for several halogen compounds incident on a hafnium filament for a source pressure $P=10^{-3}$ torr.

peratures where the response becomes slow (~ 30 sec) and the slopes turn negative.

Figures 9 and 10 show comparable plots for negative ionization of several halogen compounds on hafnium and LaB_6 filaments. In these cases the temperature range is narrow but the values of S seem to be less dependent on temperature than they are for thoriated tungsten.

Finally, Fig. 11 shows $\log S$ vs $1/T$ for tetracyanoethylene (TCNE) on three filaments of widely different work functions.

Ionization efficiencies for the molecules tested in this research on the different filaments, relative to the efficiency of ionization of potassium on rhenium (or oxygenated tungsten), are given in Table IV for three filament temperatures including that for maximum efficiency.

IV. DISCUSSION

As shown in Figs. 3 and 4 there is excellent agreement between our experimental results for the positive ionization of K on the three high work-function surfaces, rhenium, oxygenated tungsten, and depleted thoriated tungsten, and for the ionization of KCl,

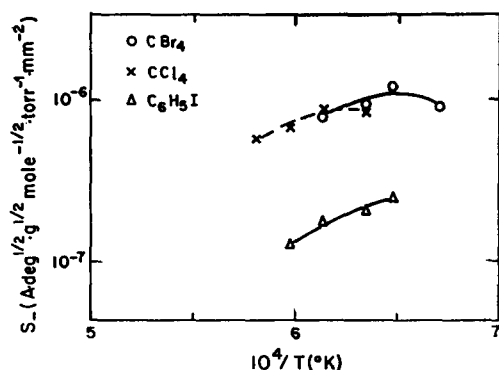


FIG. 10. Reduced ionization currents S_- of negative ions vs $1/T$ for several halogen compounds incident on a LaB_6 filament for a source pressure $P=10^{-3}$ torr.

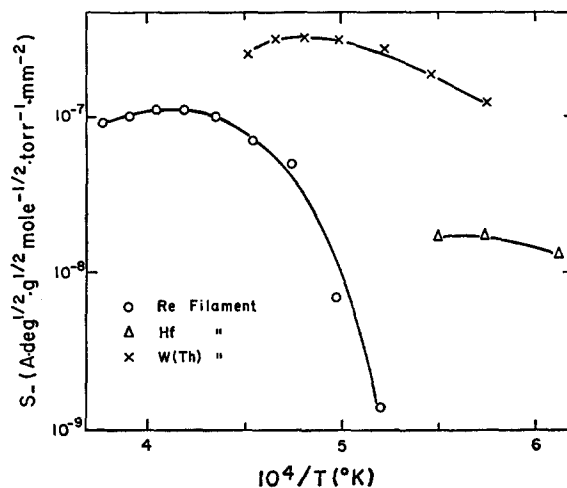


FIG. 11. Reduced ionization currents S_- of negative ions vs $1/T$ for TCNE incident on rhenium, hafnium, and activated thoriated tungsten for a source pressure $P=10^{-3}$ torr.

KBr, and KI on rhenium, over a large range of source pressures. These results agree well with the value calculated for effusion from the source and 100% ionization efficiency at the filament. This consistency shows that our method of determining relative ionization efficiencies may be reliable.

The results of our experiments fit the simple model (Saha-Langmuir equation) most closely in the case of the formation of positive ions [Eq. (4)]. The positive slopes of the plots of S vs $1/T$ (Fig. 4) for the ionization on surfaces with high work functions is consistent with $\phi > I$ (I for K is 4.339 eV¹⁷), although the accuracy of our measurements is not sufficient to permit a determination of a meaningful value for ϕ or g_{M^+}/g_M .

On thoriated tungsten surfaces with a low work function (activated) we find from the slopes of Fig. 4, $\phi = 2.65 \pm 0.1$ eV (an average value from the plots for K, KCl, KBr, and KI), in fair agreement with our value 2.8 ± 0.1 eV obtained from electron-emission measurements. If the surface is not homogeneous, the later value should weight the low ϕ part while the former weights the high ϕ part. Thus the fair agree-

TABLE V. Experimental g_{M^+}/g_M^a and g_{X^-}/g_X^b values for surface ionization on an activated thoriated-tungsten surface.

Beam molecule	g_{M^+}/g_M^a	g_{X^-}/g_X^b
K	40	...
KCl	32	4.2×10^{-5}
KBr	32	1.2×10^{-4}
KI	34	1.0×10^{-4}
Cs ^c	9.2	...

^a Calculated from the experimental data using Eq. (4).

^b Calculated from the experimental data at 1670°K assuming $\phi = 2.65$ eV.

^c Reference 21.

ment between the two shows that ϕ may be nearly constant (± 0.2 eV) over the surface.

Our results for the ionization of K on thoriated tungsten are comparable to the results of Langmuir and Kingdon²¹ for the ionization of cesium. For an activated filament they found an ionization efficiency of 0.0145 at 2160°K compared to our value of 0.0066. The value for the work function estimated from their results (Ref. 21, Table I) is 2.69 eV compared to our value 2.65 ± 0.1 eV.

Values of g_M^+/g_M , as well as g_X^-/g_X , calculated from our results (Figs. 4 and 5) for the surface ionization on thoriated tungsten are given in Table V. Table V includes also the value for the positive ionization of Cs, obtained by using the experimental data of Langmuir and Kingdon (Ref. 21, Table I). All the experimental values for g_M^+/g_M given in Table V are high compared to those ($g_M^+/g_M = \frac{1}{2}$) predicted by the Saha-Langmuir simplified model for surface ionization [Eq. (4)]. The reason for this behavior is not clear to us.

The agreement of the yields for negative ionization with the prediction of Eq. (5) is far less close than that of the positive ions with Eq. (4). The average value of ϕ obtained from the slopes of the curves of Fig. 5 is -0.4 eV. The slopes are positive as they should be if we have $\phi < \text{E.A.}$ (E.A. for Cl, Br, and I are 3.613, 3.363, and 3.063 eV, respectively²⁰), but the deviation from the value obtained for ϕ from electron-emission measurements is so great that the simple model must differ significantly from the actual situation. This is also shown by the values of g_X^-/g_X (Table V), which are calculated from the experimental data for 1670°K, assuming $\phi = 2.65$ eV. These values are much lower than those ($g_X^-/g_X \approx \frac{1}{4}$) predicted from Eq. (5).

In contrast to the behavior of the thoriated tungsten surface with respect to negative surface ionization, it is shown in Fig. 5 that the negative ionization of KCl on rhenium follows the behavior predicted by the Saha-Langmuir equation [Eq. (5)] quite well, up to a filament temperature of about 2100°K. A similar behavior was found by Fine, Madey, and Scheer²² for the surface ionization of NaCl on tungsten. Applying equations identical to our Eqs. (4) and (5), they calculated, from the observed ratios of Na⁺ ions to Cl⁻ ions at several temperatures, the work function of the surface for these temperatures. They found that the values obtained by this method are in good agreement with values obtained by electron-emission measurements. They report measurements up to a filament temperature of 2136°K. Similar results were obtained by Scheer and Fine²³ for the surface ionization of KCl, RbBr, and CsI on niobium

up to filament temperatures of about 2000°K and by Bailey²⁴ and Harden, Stelman and Muschlitz²⁵ for the ionization of halogen compounds on tungsten. These observations indicate that the alkali halide molecules do not react with rhenium, tungsten, or niobium surfaces, up to about 2100°K. The explanation for our observations in the case of thoriated tungsten may be an interaction between the halogens and thorium on the thoriated-tungsten surface. Perhaps neutral species such as ThX_n are formed and provide an alternative mechanism for removing X from the surface. Although we do not know what value of n is most important, we can make our results plausible by taking $n=1$. In place of Eq. (6b) we write

$$N = n_X + n_X + n_{mX}, \quad (14)$$

where mX is a diatomic molecule formed by one halogen atom X from the beam and one metal atom m from the surface. Equation (5) is now modified to

$$\frac{n_X^-}{n_X + n_{mX}} = \frac{g_X^- \exp[(\text{E.A.} - \phi)/kT]}{g_X \{1 + (g_{mX}/g_X) \exp[D(mX) - \Delta E_{vap}(m)]/kT\}}, \quad (15)$$

where g_{mX} and $D(mX)$ are, respectively, the statistical weight and dissociation energy of mX and $\Delta E_{vap}(m)$ is the energy of vaporization of m. The derivation of the expanded part of the denominator of Eq. (15) exactly parallels the derivation of Eq. (5) with an atom m taking the place of an electron. We estimate g_{mX} from typical values of the vibrational and rotational partition functions for a diatomic molecule to be about 10^4 – 10^6 at 1700°K. Although we have not found reliable data for all the $\Delta E_{vap}(m)$ or for most of the $D(mX)$ for the metals discussed here, approximate values show that n_{mX}/n_X is probably less than 10^{-5} for Nb, W, and Re, while it may be in the range of 10 – 10^3 for Hf, Th, and LaB₆ (or La). It is possible that similar chemical interactions are the cause also for the decrease in the negative ionization efficiency of KCl on rhenium above a filament temperature of 2100°K.

Trischka, Marple, and White²⁶ studied the ionization of CsCl, CsBr, and CsI on thoriated tungsten. They obtained the efficiencies for negative ionization by assuming that the efficiencies of positive ionization on deactivated thoriated tungsten are 1.0. The efficiencies for the production of negative ions that they report (0.30 for CsCl, 0.11 for CsBr, and 0.02 for CsI, independent of temperature between 1200

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²³ M. D. Scheer and J. Fine, J. Chem. Phys. **43**, 3645 (1965).

²⁴ T. L. Bailey, J. Chem. Phys. **28**, 792 (1958).

²⁵ C. S. Harden, D. Stelman, and E. E. Muschlitz, Jr., Proc. Conf. ASTM 14th, Dallas, Tex., 1966, p. 61.

²⁶ J. W. Trischka, D. T. F. Marple, and A. White, Phys. Rev. **85**, 136 (1952).

and 1500°K) are about 10 times higher than our observations for the corresponding potassium halides at 1620°K (Table IV). This difference may be partly explainable in terms of differences in the probability of accommodation of cesium and potassium halides on the thoriated surface. Another possible explanation of the different efficiencies observed is that the thoriated tungsten in Ref. 26 may not have been entirely deactivated during the measurements of the positive ionization. If this was the case, the actual efficiency would have been lower than the assumed value of 1.0, and as a result the calculated negative ionization efficiencies would have been too high.

Figures 6-8 describe the results obtained for a wide range of bond types for halogen compounds, from covalent to largely ionic, ionized on thoriated tungsten. The values of β are again much lower than predicted by Eq. (5) but consistent with Eq. (15). The dependence of ionization efficiencies on the number and type of halogen atoms in the molecule is not very clear. In general the efficiency tends to become larger as the number of halogen atoms in the molecule increases. Thus we have

$$\beta(\text{CBr}_4) \approx 3\beta(\text{Br}_2) \approx 14\beta(\text{C}_6\text{H}_5\text{Br}),$$

$$\beta(\text{CCl}_4) \approx 6\beta(\text{C}_6\text{H}_5\text{Cl}),$$

$$\beta(\text{I}_2) \approx 4\beta(\text{C}_6\text{H}_5\text{I}) \approx 8\beta(\text{C}_2\text{H}_5\text{I}).$$

But there are many exceptions, for example we note $\beta(\text{C}_2\text{Cl}_6) \approx \frac{1}{2}\beta(\text{C}_6\text{H}_5\text{Cl})$, $\beta(\text{KCl}) \approx 10\beta(\text{C}_6\text{H}_5\text{Cl})$, and $\beta(\text{HI}) \approx \frac{1}{8}\beta(\text{C}_6\text{H}_5\text{I})$. The dependence on the type of halogen in the molecule is much smaller than that predicted by Eq. (5) but may be rationalized on the basis of Eq. (15). Thus the efficiency of ionization of Br_2 is of the same order as for I_2 , and the efficiency for CCl_4 is of the same order as for CBr_4 . For the halobenzenes

$$\beta(\text{C}_6\text{H}_5\text{Cl}) \approx 2\beta(\text{C}_6\text{H}_5\text{Br}) \approx 2\beta(\text{C}_6\text{H}_5\text{I}).$$

The yields of negative ions on hafnium are much lower (by a factor of 10-70) than they are for the same compounds on thoriated tungsten. This is consistent with the prediction of the Saha-Langmuir model since hafnium has a higher work function.

Here again Eq. (15) can explain the low ion yields which are below those predicted from Eq. (5) by a factor of 10^2 - 10^8 . Because of the small yields of negative ions on hafnium, measurements were done only over a small range of filament temperatures, and therefore we cannot estimate the work function of the surface from our surface-ionization results.

The dependence of the efficiency on number and type of halogen atoms in the molecule is less confusing than for thoriated tungsten, e.g., $\beta(\text{CCl}_4) \approx 4\beta(\text{C}_6\text{H}_5\text{Cl})$, $\beta(\text{I}_2) \approx 2\beta(\text{C}_6\text{H}_5\text{I})$, $\beta(\text{CCl}_4) \approx 2.5\beta(\text{CBr}_4)$, $\beta(\text{Br}_2) \approx 8\beta(\text{I}_2)$, and $\beta(\text{C}_6\text{H}_5\text{Cl}) \approx 6\beta(\text{C}_6\text{H}_5\text{I})$.

The yields of negative ions on the LaB_6 filament are of the same order of magnitude as on the thoriated tungsten, but the uncertainty is much bigger because of our difficulty in estimating the fraction of the surface of the rhenium support effectively covered by LaB_6 .

The latest value for the electron affinity of tetracyanoethylene (TCNE) is 2.89 eV.²⁷ Because mass-spectrometric studies²⁸ showed that the only negative ion formed on Pt in $(\text{TCNE})^-$, we can suspect that this molecule does not break up into fragments (e.g., CN^- with E.A., 3.8 eV) on our filaments. Application of Eq. (5) to our experimental results for TCNE gives $g-/g_{\text{neutral}}$ approximately 14 on Re at 2000°K, 0.08 on Hf at 1667°K, and 3×10^{-3} on W(Th) at 1850°K. Possibly there is little interaction of TCNE with Re atoms on the surface but increasing interaction with Hf and Th.

In view of the results reported here, it seems that of the filaments tested by us thoriated tungsten is the most satisfactory for negative ionization. The efficiencies for ionization on this surface look good enough that it might be used in a detector for some molecular-beams studies.

ACKNOWLEDGMENTS

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²⁸J. T. Herron, H. M. Rosenstock, and W. R. Shields, Nature **206**, 611 (1965).