DETERMINATION OF THE IONIZATION POTENTIAL OF URANIUM BY A SURFACE IONIZATION METHOD

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A method is described for determining the difference in ionization potentials for two different atomic species which are ionized simultaneously on a heated metal surface. The method has been verified by measuring the ionization potentials of sodium and lithium. The method has been used to measure the difference in ionization potentials of uranium and lithium. The ionization potential of uranium is found to be 6.08 ± 0.08 volts. At high temperatures the positive ion currents for sodium, lithium, and uranium are found to vary in accordance with the theoretical expressions for surface ionization.

The most precise values of the ionization potentials of atoms (V) are obtained from atomic spectra. In a number of cases, however, for instance the rare earths and uranium, atomic spectroscopy has not yet furnished reliable values of V. In the present paper we describe a method for determining the difference in ionization potentials for any two atomic species which can be ionized on a heated metallic surface. The method is based on a comparison of the ion currents of the two elements which are ionized simultaneously on the same heated surface; this scheme has been used by us earlier 1 for determining the difference in electron affinities for atoms which are capable of forming negative ions by means of surface ionization.

Usually surface ionization is investigated with heated polycrystalline filaments of refractory metals. It is known that the surfaces of such filaments exhibit an inherent nonuniformity in work function — different grains have work functions which differ significantly. 2 The adsorption of contaminating atoms on the surface may lead to an increase in the nonuniformity in contact effects at the surface. If the intensity of the electric field E which extracts ions from the surface is sufficient to compensate for the contact field of these localized regions the ion emission of the surface is the simple sum of the ion currents for all such localized regions.* The work function of all the regions lies within the limits \( \varphi_{k \min} \) and \( \varphi_{k \max} \). It has been shown, 3 that if the following condition is satisfied:

\[
\varepsilon (V - \varphi_{k \max} - V \varepsilon E) \gg kT
\]

the surface ionization coefficient \( \beta \) of such a non-uniform surface is

\[
\beta = n^+ / n = A \exp (\varepsilon / kT) \left( V \varepsilon E - V \right) \times \sum_k f_k \exp (\varepsilon \varphi_k / kT).
\]

Here \( n \) is the number of atoms which strike the surface per second, \( n^+ \) is the number of positive ions which are extracted from the surface per second; \( A \) is the ratio of the partition functions of the ions and atoms; \( f_k \) is the area of all regions of the k-th type which have a work function \( \varphi_k \); \( T \) is the temperature of the surface and \( \varepsilon \) is the charge of the electron.

Assuming that two atomic species are ionized simultaneously on the same surface, using Eq. (2) we obtain the ratio of ion currents

\[
I_1 / I_2 = (A_1 n_1 / A_2 n_2) \exp \left( (\varepsilon / kT) (V_2 - V_1) \right) \]

or

\[
\log \left( I_1 / I_2 \right) = \log \left( A_1 n_1 / A_2 n_2 \right) + 5040 (V_2 - V_1) T^{-1}.
\]

If the condition in (1) is satisfied the ion-current ratio \( I_1 / I_2 \) is independent of the state of the surface and the intensity of the ion accelerating field \( E \).

Equations (3) and (4) may be used to determine the difference in ionization potentials \( \Delta V = V_2 - V_1 \) of two elements. Knowing the ionization potential of one of the elements it is then possible to deter-
mine the ionization potential of the other. Two methods can be used for this purpose: the ratios $n_1/n_2$ and $I_1/I_2$ can be determined experimentally at different values of $T$ and the quantity $\Delta V = V_2 - V_1$ calculated from Eq. (3) or the quantities $n_1$ and $n_2$ can be held constant throughout the experiment and the function $\log I_1/I_2 = f(1/T)$ determined, thereby making it possible to determine $\Delta V$ from the slope of the curve. The quantities $A_1$ and $A_2$ remain essentially constant for small variations of $T$ and are known for the majority of elements.

Equation (2) can also be written in the form

$$I = nA^* \exp \left[ (\varphi^* + \varphi - V) / kT \right]$$

where $A^* = \Sigma k f_k \exp \left[ (\epsilon / kT) (\varphi_k - \varphi^*) \right]$ is a weak function of $T$. For small variations of $T$ the quantity $A^*$ is essentially constant. In this case the curve $\log I = f(1/T)$ should be a straight line, the slope of which should yield the quantity $\varphi^* + \sqrt{\epsilon} - V$. If $\varphi^*$ is the same for ionization of different elements on the same surface the condition in (1) is actually satisfied.

**METHOD OF MEASUREMENT**

In order to make separate measurements of the ion currents for the two atoms and to exclude effects due to easily ionized contaminants the experiments are carried out in a magnetic-sector mass spectrometer. The filament on which surface ionization is investigated serves as the ion source of the mass spectrometer.

The atoms of the elements being compared are directed onto the filament $H$ (Fig. 1) through symmetrically arranged slits $S_1$ and $S_2$ from two evaporators $E_1$ and $E_2$. Slits $S_1$ and $S_2$ can be closed independently by means of slides. The ions from the filament are accelerated by means of an electric field (the potential difference between the filament and the accelerating electrode is $600 - 1,000$ volts) in the direction of the input slit ($S$) of the mass spectrometer and the ion beam, which is mass resolved in the magnetic field, strikes the detector. The ion currents are measured with a type EMU-3 electrometer amplifier, sometimes in conjunction with a secondary-electron multiplier. During the measurements the vacuum in the device is never worse than $10^{-6}$ mm Hg. Before the measurements are made the filament is baked; the filament temperature is measured with an optical pyrometer.

In order to check the method $\Delta V$ was measured in sodium and lithium, the ionization potentials of which are well-known ($5.14$ and $5.40$ volts respectively). Since it is possible that (1) is not satisfied for ionization of Na on W, the ionization of sodium and lithium was studied on tantalum filaments. Having convinced ourselves from this work that the method was satisfactory we then determined the difference in ionization potentials for uranium and lithium. The effect was studied with tungsten filaments in the latter elements.

The reason for using tungsten instead of tantalum to measure the ionization potentials for lithium and uranium is the following. Uranium is rather strongly adsorbed by surfaces and remains on these surfaces even when heated to $2300^\circ$K and higher. When tantalum or tungsten is covered by uranium the work function of these materials is reduced sharply. In order to guarantee the maximum purity of the surface for the range of values of $T$, it is necessary to carry out the measurements of $I = f(t)$ at the highest possible temperatures. When tungsten is used it is possible to raise $T$ up to $2800^\circ$K. To reduce contamination of the surface by uranium in the operating temperature range it is convenient to reduce the number of uranium atoms which strike the filament; however this procedure obviously leads to a reduction in ion current. By using an electron multiplier as a preamplifier the sensitivity is increased by two orders of magnitude; in some of the experiments this increase allows us to make a corresponding reduction in the intensity of the molecular beams from the ovens.

We have not studied ionization in the pure metals, but rather in halogen salts NaCl, LiCl, LiF, UC14, and UF4, which are simpler for experimental purposes. It is assumed that at the operating temperatures complete reduction of the metals obtains at the surface. A great deal of attention is given to the problem of making the intensity of the molecular beams constant. The evaporating ovens have a thermal inertia and the heating elements are supplied by high-capacity storage batteries. Before the measurements the
The oven temperature is established at 2250°K for tantalum and 2650°K for tungsten. Successive measurements are made of the current of F⁺ ions for ionization of LiF and UF₄ (the molecular beams are shut off by the oven slides) or the chlorine isotopes in the case of NaCl—LiCl and LiCl—UCl₄: the additivity of the currents when both slides are opened and the stability of the currents are checked. In making the calculations, in accordance with Eq. (4) it is assumed that the ratio \( n_1/n_2 \) is equal to the ratio of the negative ion currents of chlorine for the NaCl—LiCl case or \( \gamma_C \) of the ratio of the negative ion currents for UCl₄—LiCl and UF₄—LiF. Then the magnetic and accelerating electric fields are reversed and at the same temperature \( T \) measurements are made of the positive ion currents \( I_1 \) and \( I_2 \). In all the subsequent measurements at other values of \( T \) the stability of the molecular beams is checked periodically at 2250°K for tantalum and 2650°K for tungsten.

**Second method.** In this case measurements are made of the dependence of the positive ion currents on \( T \) and graphs of the function \( \log (I_1/I_2) = f(1/T) \) are plotted. The values of \( n_1 \) and \( n_2 \) and the intensities of the molecular beams are monitored by measuring the currents of positive ions at \( T \) equal to 2250°K for Ta and 2650°K for W; the currents are measured before and after the measurements at each temperature.

**RESULTS OF THE MEASUREMENTS**

Curves of the function \( \log (I_1/I_2) = f(1/T) \) are shown in Fig. 2 for ionization of Li and Na on tantalum; it is apparent from these curves that, in agreement with Eq. (5), the experimental points lie on a straight line in the temperature range from 1700 to 2375°K. From the slope of the straight lines we find \( \phi^* + \sqrt{\varepsilon E} - V \) is 0.53 volts for Na and 0.83 volts for Li. In both cases this gives agreement with the limits of experimental accuracy for the values of \( \phi^* + \sqrt{\varepsilon E} \) (to 4.61 and 4.57 volts).

All the lines have been plotted from the experimental data, using a least-squares fit. Approximately 85 determinations were made of the differences in ionization potentials of lithium and sodium \( V_{Li} - V_{Na} \) by the first method in different samples of tantalum for values of \( T \) between 1600 and 2115°K (with different values of the intensities of the molecular beams of NaCl and LiCl). The spread in the values of \( \Delta V \) is found to lie between 0.23 and 0.28 volts while the mean arithmetic value of 85 determinations yields \( V_{Li} - V_{Na} = 0.25 \pm 0.02 \) volts.

In addition two series of measurements were made by the second method in the temperature range between 1700 and 2375°K. An example of a curve \( \log (I_1/I_2) = f(1/T) \) is shown in Fig. 3. The values of \( \Delta V \) calculated from ten curves lie between the limits of 0.19 and 0.32 volts. The average of all the values is found to be \( V_{Li} - V_{Na} = 0.26 \pm 0.05 \) volts. The results obtained by both methods are in agreement with the spectroscopic data for these elements.

In making a comparison of the ion currents \( U - Li \) we cannot use the first method because of the difficulty of making an accurate determination of the ratio of ion currents \( I_U/I_{Li} \) in this case. In determining \( I_U/I_{Li} \) it is necessary to make corrections for the difference in the ion-electron emission coefficients for \( U^+ \) and \( Li^+ \) at the first dynode of the multiplier and for the difference in the transmission of the mass spectrometer in the passage of ion beams which differ so greatly in mass.

In Fig. 4 we show the function \( \log (I_1/I_{2250}) = f(1/T) \) for Li and U for ionization of the salts LiF and UF₄ on tungsten in the temperature region between 2100 and 2800°K. In all cases the straight lines reproduce the behavior of the experimental functions. In Fig. 5 is shown the curve \( \log (I_{Li}/I_U) = f(1/T) \); the slope of this curve can be used to calculate \( V_U - V_{Li} \).

Varying the experimental conditions we carried out five series of measurements of the temperature dependence of the ion currents in the ioniza-
tion of $\text{UF}_4 - \text{LiF}$ and one in the ionization of $\text{UCl}_4 - \text{LiCl}$; the appropriate curves were plotted. The differences $V_U - V_{\text{Li}}$ determined from the slope lie between 0.57 and 0.83 volts while the average value if $V_U - V_{\text{Li}} = 0.68 \pm 0.08$ volts. Whence the ionization potential of the uranium atom is

$$V_U = 5.40 \pm 0.68 = 6.08 \pm 0.08 \text{ V}.$$  

The uncertainty in the determination of $\Delta V$ stems from the estimate of the accuracy of the determination by Eq. (4). Actually the ratio of the ion currents in the mass spectrometer is measured with an accuracy which is probably no better than $10 - 20\%$. The basic reason for the reduction in the accuracy of the current measurements is the small uncontrollable shift of the filament with respect to the input slit of the mass spectrometer as the temperature is changed. The molecular beam intensity is maintained with an accuracy of several percent during the experiments. The accuracy in the measurement of $T$, which is carried out by means of an optical pyrometer, is $2 - 3\%$.

Our assumption as to the complete dissociation of the molecules of the alkali-halide salts on tungsten and tantalum surfaces is rather well justified by all of the work which has been carried out on the surface ionization of these salts. The reduction of the uranium and certain other rare metals from the halogen salts at high temperatures is used in metallurgy in order to obtain pure metals. The agreement of the experimental relations $I = f(T)$ in Figs. 2 and 4 with Eq. (5) appears as additional evidence for the complete dissociation of the salts used in the present work.


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