

## ON THE MECHANISM OF SURFACE IONIZATION OF ATOMS OF THE ALKALI EARTH METALS

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The concurrent surface ionization of the alkali earth metals (barium, strontium, calcium, and magnesium) and an alkali metal (sodium) on incandescent tungsten was investigated with a mass spectrometer. The ionization coefficients were found to be significantly higher when oxygen was circulated over the tungsten. The results obtained are explained on the basis of the Saha-Langmuir theory. The specific character of the ionization of alkali-earth metals when the tungsten is oxidized is related to the evaporation of molecules of the oxides of these metals from the surface.

POSITIVE surface ionization was investigated thoroughly only for alkali metals. The experimental data agree in this case satisfactorily with the Saha-Langmuir theory.<sup>1-4</sup> The results of the relatively small number of investigations with the alkali-earth metals, which furthermore were not carried out under identical conditions, cannot be interpreted unambiguously.

It was established by Starodubtsev and Timokhina,<sup>5</sup> who used a mass-spectrometric procedure to investigate concurrent surface ionization of magnesium and sodium, that the temperature variation of the ion currents from pure tungsten corresponds approximately to the Saha-Langmuir theory. However, the estimated ionization coefficients for magnesium were found to be considerably higher than the theoretical ones. Morozov<sup>6</sup> in his experiments on barium observed no great deviations from the theory in the high-temperature region, while at low temperatures the results were affected by inadequate vacuum conditions. Along with this, Dobretsov, Starodubtsev, and Timokhina<sup>7</sup> have observed, in an investigation of the ionization of calcium and magnesium on tungsten coated with a thin layer of oxides of these elements, unique phenomena which do not lend themselves to a simple interpretation.

In our own paper<sup>8</sup> we cited several results of a mass-spectrometric investigation of the surface ionization of strontium, calcium, and manganese, results that found use in the measurement of the magnetic moments of nuclei by means of magnetic resonance in molecular beams.<sup>9</sup> Further experiments have supplemented and refined these results and have made it possible to explain the mechanism of the phenomenon. The experiments were carried out with a mass-spectrometric detector of molec-

ular beams.<sup>10</sup> The measurement procedure is analogous to that described in reference 5.

Typical temperature characteristics of concurrent surface ionization of Ba, Sr, Ca, Mg, and the alkali metal Na, used for comparison, on a highly-incandescent tungsten filament, upon simultaneous evaporation of the metals from various furnaces, are shown in Fig. 1. At filament temperatures ranging from 1600 to 2200°K, the logarithms of the ion currents of the investigated elements are approximately linear in  $1/T$ , while the values of the effective work function of tungsten, calculated by the Saha-Langmuir formula from the slopes of the lines, had a spread ranging from 4.6 to 4.8 volts for different elements and in different experiments. The coefficients of surface ionization, estimated from the values of the ion current, from the temperature of the calibrated-slit furnace temperature, and from the geometry of the instrument are of the same order of magnitude as the theoretical ones. Taking into account the "spotty" structure of the surface of the metallic filament, the results obtained can be explained on the basis of the Saha-Langmuir theory.

As is well known, a considerable increase in the coefficient of surface ionization for alkali metals can be attained upon oxidation of the tung-

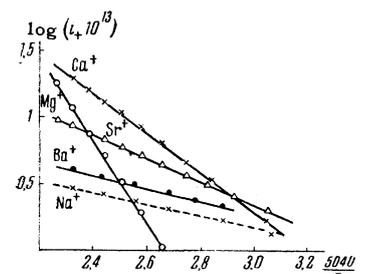


FIG. 1. Temperature characteristics of ion currents from pure tungsten ( $i_+$  amperes).

sten by increasing the work function. However, at temperatures above 1600°K, necessary for the evaporation of the adsorbed atoms of the alkali-earth metals, the oxygen film on the tungsten becomes unstable.

A considerable and stable increase in the effectiveness of the ionization in the high-temperature range is observed during continuous oxidation of tungsten in a stream of oxygen.<sup>8</sup> However, this method does not make it possible to compensate fully for the desorption of oxygen from the surface, owing to the partial destruction of the oxygen film by the oxygen molecules formed when the volatile tungsten oxide WO<sub>3</sub> interacts with this film.<sup>11</sup> One can therefore expect that under increased oxygen pressure, the oxygen film on the tungsten and accordingly the work function will tend to limiting values, determined by the filament temperature.

The dependence of the Na and Sr ion currents on the oxygen pressure in a system operating at constant filament temperature (Fig. 2) confirms,

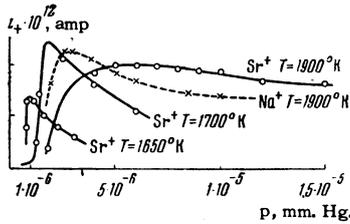


FIG. 2. Dependence of the ion currents of Sr and Na on the oxygen pressure.

in general outline, this hypothesis. Certain reductions in the Na and Sr ion currents at  $T = 1900^\circ\text{K}$  in the high-pressure region can be naturally attributed to scattering of the atomic and ion beams by the oxygen. It is interesting that as the temperature of the filament drops, the curves for Sr, unlike those for Na, drop ever more rapidly with increasing pressure. This effect is particularly pronounced in the case of Ba.

At a constant inflow of oxygen, the ion current of Na monotonically increases with diminishing temperature, reaching saturation at  $T < 1600^\circ$  (Fig. 3). Thanks to the stability of the oxygen film on the tungsten at such temperatures, the cessation of oxygen flow no longer causes a re-

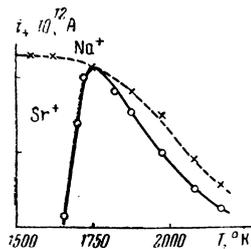


FIG. 3. Temperature dependence of the ion currents of Sr and Na from oxidized tungsten. Oxygen pressure  $p = 3.5 \times 10^{-6}$  mm. Hg.

duction in the sodium ion current. The strontium ion current at  $T > 1800^\circ\text{K}$  behaves similar to sodium in a qualitative way, but it drops sharply at lower temperatures. An analogous situation is observed for the other alkali-earth metals (Fig. 4).

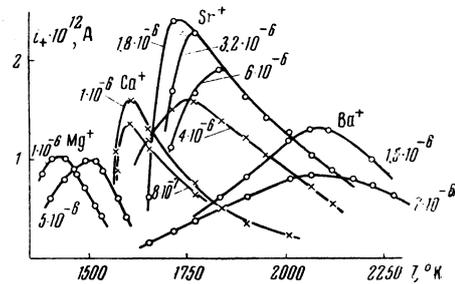


FIG. 4. Temperature dependence of the ion currents of Ba, Sr, Ca, and Mg from oxidized tungsten. The oxygen pressure in mm. Hg. is indicated on the diagram.

For an identical inflow of oxygen, the positions of the maxima of the ion currents are arranged in order of increasing atomic numbers of the elements. As the oxygen pressure is increased, the maxima shift towards the higher temperatures. In the high-temperature region, beyond the maximum of the ion current vs. temperature curve, the ionization coefficients increase with inflow of oxygen to an equal degree for all of the investigated elements.

The foregoing results have a natural explanation, if it is assumed that the Saha-Langmuir theory is applicable in the foregoing region of high temperatures. As the temperature is reduced from the maximum, the ion-current exhibits considerable inertia, as manifest by rapid variations of filament temperature or rapid variations of the intensity of the atomic beam. This inertia is due to the long lifetime of the atoms on the film. Figure 5 shows curves of the logarithm of the time (in seconds), during which the ion current is reduced by  $1/2$  after a sudden blocking of the atomic beam, vs.  $1/T$ . Under these conditions, the surface ionization of alkali-earth metals assumes a clearly pronounced specific character. The sharp reduction in the ion current with decreasing tem-

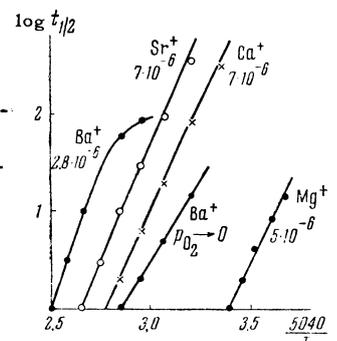


FIG. 5. Temperature characteristics of the lifetimes of the atoms on the filament. The oxygen pressure  $P_{O_2}$  is indicated on the curves in mm. Hg.

perature (Figs. 3 and 4) and with increasing pressure of oxygen (Fig. 2), not observed for sodium, cannot be attributed to a reduction in the work function by the adsorbed atoms of the alkali-earth metals, for example, because an analogous situation is observed at a very weak atomic-beam intensity and correspondingly at negligibly small equilibrium covering of the surface by the adsorbed atoms. Nor can we accept an explanation that brings into play the surface diffusion of the adsorbed atoms. If the coefficients of diffusion over the surface of the tungsten are taken into account,<sup>12</sup> the time necessary to go beyond the limits of the effective section of the ionizer filament is several orders of magnitude greater than the mean lifetimes of the atoms on the filament.

The most probable premise is that the peculiarities of surface ionization of alkali-earth metals are due to a possible formation of molecules of the oxides of these metals on the surface, followed by evaporation of these molecules. Similar phenomena take place in surface ionization of rare-earth elements and actinides, where ions of the oxides are observed directly along with the atomic ions.<sup>13-16</sup> In our experiments, the ions  $\text{BaO}^+$  and  $\text{SrO}^+$  were observed when the ion source of the detector operated in a mode wherein volume ionization of the gas molecules was produced by the electrons emitted by the filament. The formation and evaporation of oxides should play an increasing role with increasing oxygen pressure and with decreasing filament temperature, leading to a decrease in the yield of atoms from the surface. Retaining the premises of the Saha-Langmuir theory as regards the surface ionization of the atoms, we can explain qualitatively the anomalous drop in the ion currents observed under these conditions for alkali-earth metals.

In conclusion, I express my deep gratitude to Prof. V. Hartman for guidance in the initial stage of the investigation, to A. G. Kucheryaev and Sh. M. Gogichaishvili for help with the work, and to A. M. Romanov for valuable critical comments.

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