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Abstract

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PHYSICS

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DETERMINATION OF THE ELECTRON-AFFINITY ENERGY OF COPPER, SILVER, AND GOLD ATOMS BY THE METHOD OF SURFACE IONIZATION

(Presented by Academician B. P. Konstantinov, 30 X 1963)

As was already noted in one of the preceding articles (^{1}), the experimental possibilities currently available make it possible to observe negative surface ionization of all elements whose atomic electron-affinity energy exceeds 1 eV. On the basis of indirect estimates, the elements of subgroup II of group I of the Mendeleev periodic system—Cu, Ag, Au—were also assigned to such elements.

Indeed, we succeeded in observing appreciable currents of negative ions Cu^-, Ag^-, Au^- during surface ionization of vapors of these elements on a polycrystalline tungsten filament heated to a temperature of 1800–2300° K. To determine the electron-affinity energy S of the atoms Cu, Ag, Au, the previously described method of comparing the currents of negative ions of two elements was used. If fluxes n_1 and n_2 of atoms of the elements under investigation simultaneously arrive at a surface heated to temperature T, then the ratio of the currents of negative ions of these elements I_1/I_2, under fulfillment of the condition (^{2})

$$\varepsilon(\varphi_{\min} - S) \gg kT \tag{1}$$

is expressed by the relation

$$\frac{I_1}{I_2} = \frac{n_1 A_1}{n_2 A_2} \exp \frac{\varepsilon(S_1 - S_2)}{kT}, \tag{2}$$

where ε is the electron charge; k is Boltzmann' s constant; $\varphi_{\min}$ is the minimum value of the local work function of the surface; A_1 and A_2 are the ratios of the statistical sums of the ionic and atomic states. The difference of the values $S_1 - S_2$ can be calculated from formula (2) by experimentally measuring the ratios I_1/I_2 and n_1/n_2 at the filament temperature T. It is also possible to

Fig. 1

Figure 1: Fig. 1

determine $S_1 - S_2$ from the slope of the graph $\lg(I_1/I_2) = f(1/T)$, if n_1 and n_2 are kept constant during the experiment.

Experimental results

The experimental procedure was described earlier (^{1}). Molecular beams of the elements under investigation were directed onto a heated tungsten filament 0.1 mm in diameter from two independent evaporators. Metallic copper, silver, or gold was placed in one of the evaporators, and the salt KJ in the other. The KJ molecules, as is known, dissociate completely on the surface of heated tungsten and desorb from it in the form of atoms and atomic ions. The tungsten filament was placed in front of the entrance slit of a magnetic sector mass spectrometer. The ion currents were measured with a secondary-electron multiplier connected to the input of an electrometric amplifier. Such a system made it possible to measure ion currents down to 10^{-17} A. Measurements of the ion currents were carried out in the temperature interval 1800–2300° K; the filament temperature was measured with an optical pyrometer.

The pressure of the residual gases in the apparatus during the experiments did not exceed 10^{-6} torr.

The difference between the electron-affinity energies of iodine atoms and of the element under study was determined from the slope of the plot $\lg(I_1/I_2) = f(1/T)$. The constancy of the molecular fluxes onto the filament from the evaporators was monitored during the experiment by the invariability of the ion currents recorded by the mass spectrometer at the highest filament temperature. In Fig. 1 the plots of $\lg(I_1/I_2)$ versus the reciprocal filament temperature are shown. The experimental points are satisfactorily approximated by straight lines, from the slopes of which, in accordance with formula (2), the values of the differences $S_1 - S_2$ were found. For each element no fewer than five independent measurements of the dependence $\lg(I_1/I_2) = f(1/T)$ were carried out. The averages of the values found for $S_1 - S_2$ are given in Table 1.

Fig. 1

The magnitude of the electron affinity of iodine was determined recently with high accuracy in experiments on the study of the absorption spectra of negative ions in vapors of alkali-halide salts formed behind the front of a shock wave (^{3}), and in experiments on the investigation of the photodetachment of electrons from negative iodine ions (^{4}). The value $S(\mathrm{J}) = 3.07$ eV obtained in these experiments was used to calculate the electron-affinity energies of copper, silver, and gold atoms (Table 1). The deviations of individual determinations of the quantity S from the mean values given in the table are greatest in the case of copper, for which the quantity $S_1 - S_2$ has the largest value. The principal reason for the relatively large scatter of the values obtained is apparently connected with the insufficient accuracy, in our experiments, of determining the filament temperature by means of a technical optical pyrometer.

In addition to comparing the ion currents of the elements under study with the current of negative iodine ions, as a control experiment the dependence $\lg(I_{\mathrm{Ag}}/I_{\mathrm{Au}}) = f(1/T)$ was measured during simultaneous ionization of silver and gold atoms on the surface of a tungsten filament. In agreement with the data of Table 1, the value of $S_1 - S_2$, found from the slope of the plot $\lg(I_1/I_2) = f(1/T)$, proved to be equal to ~ 1 eV.

Table 1

Element X	$[S(\mathrm{J}) - S(X)]$, eV	$S(X)$, if $S(\mathrm{J}) = 3.07$ eV
Cu	1.6 ± 0.5	1.5 ± 0.5
Ag	1.07 ± 0.2	2.0 ± 0.2
Au	0.27 ± 0.1	2.8 ± 0.1

In the study of the surface ionization of copper and silver, one more method was used for estimating the electron affinity. Since the ionization potentials V of Cu and Ag atoms are equal, respectively, to 7.72 and 7.57 eV, on the surface of heated tungsten the formation is possible not only of negative, but also of positive ions of these elements. Then, if the conditions (1) and

$$\varepsilon(\nu - \varphi_{\max}) \gg kT, \tag{3}$$

are satisfied, the ratio of the currents of positive and negative ions can be written in the following form (^{2}):

$$\frac{I_+}{I_-} = \frac{A_+ \exp \frac{\varepsilon(\varphi_+ - V)}{kT}}{A_- \exp \frac{\varepsilon(S - \varphi_-)}{kT}}. \tag{4}$$

This method is less reliable than the one described above, since in order to determine S it is necessary to know the values of the effective work functions for the formation of positive and negative ions on a pyritized surface, φ_+ and φ_-, as well as the absolute value of the current ratio I_+/I_-. The quantities φ_+ and φ_- were estimated from the slope of the dependences $\lg I = f(1/T)$ for the current of positive ions Cu^+ and Ag^+ and the current of negative iodine ions, and amounted to $\varphi_+ = 5.2 \div 5.3$ eV and $\varphi_- = 4.9 \div 5.0$ eV. In measuring the ratio I_+/I_-, the ion-electron emission coefficients of the first dynode of the multiplier for positive and negative ions were taken to be identical, which apparently may lead to additional errors. The values of S found from formula (4) for a number of filament temperatures lie within the ranges: $S(\mathrm{Cu}) = 2.1 \div 2.2$ eV and $S(\mathrm{Ag}) = 2.0 \div 2.3$ eV. These values do not contradict those given in Table 1.

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Note: Figure translations are in progress. See original paper for figures.