Physics

I. N. Bakulina and N. I. Ionov

1957

SovietRxiv

Abstract

Full Text

Physics

I. N. Bakulina and N. I. Ionov

Determination of the Electron-Affinity Energy of Sulfur Atoms by the Method of Surface Ionization

(Presented by Academician A. A. Lebedev on 27 IV 1957)

In a previous article (1) we described experiments on the surface ionization of potassium rhodanide (KCNS) molecules on tungsten, in which the formation of negative ions of the radical CN^- and of atoms S^- was observed. A very rough estimate was made of the electron-affinity energy of sulfur atoms, showing that this quantity is approximately 2 eV.

In the present article, experiments are described that made it possible to determine the electron-affinity energy of the sulfur atom with greater reliability.

The method used for determining electron affinity had been used by us earlier (2). It is based on comparing the currents of negative ions of two elements ionized simultaneously on one and the same surface.

As is known, the magnitude of the current I of negative ions from an ionizing surface is determined by the following formula:

$$I = \frac{n\varepsilon}{1 + \dfrac{g_a}{g_p} e^{\frac{\varepsilon(\varphi - s)}{kT}}}, \tag{1}$$

where n is the number of atoms arriving at the surface per unit time; T is the surface temperature; s is the electron-affinity energy of the atoms; φ is the work function of the surface; g_p and g_a are the statistical weights of the element in the ionic and atomic states, respectively; k is Boltzmann' s constant; ε is the electron charge. We studied ionization on the surface of a polycrystalline tungsten filament, the work function of whose individual regions may vary within rather wide limits between $\varphi_{\min}$ and $\varphi_{\max}$. However, the electron-affinity energy even of the most electronegative atoms, for example halogen atoms, in the case of pure tungsten is so much smaller than $\varphi_{\min}$ that at all possible tungsten temperatures one may neglect unity in the denominator of formula (1) in comparison with the second exponential term. In this case formula (1) takes the form:

$$I \simeq n\varepsilon \frac{g_p}{g_a} e^{\frac{\varepsilon(s - \varphi)}{kT}}. \tag{2}$$

Fig. 1

Figure 1: Fig. 1

If n_1 atoms of one element and n_2 atoms of another element fall on one and the same surface per unit time, then, by experimentally measuring the ratio of the currents I_1/I_2 of the negative ions of these elements from the surface and the surface temperature T, one can determine the difference of the energies

electron affinity of the ionizing atoms by the following formula:

$$\frac{I_1}{I_2} = \frac{n_1}{n_2}\frac{A_2}{A_1}e^{\frac{\varepsilon(S_1-S_2)}{kT}}, \tag{3}$$

whence

$$S_1 - S_2 = \frac{T}{5040}\left[\lg\frac{I_1}{I_2} + \lg\frac{n_2 A_2}{n_1 A_1}\right], \tag{4}$$

where $A_1 = g_{a1}/g_{p1}$, $A_2 = g_{a2}/g_{p2}$.

Thus, knowing the electron-affinity energy of one element, one can determine its value for another element being compared.

In the present work we determined the differences between the electron-affinity energies of bromine and sulfur atoms by studying the surface ionization of sodium bromide (NaBr) and sodium sulfide (Na_2S) molecules. For this purpose, as previously ([2]), molecular beams of NaBr and Na_2S from two independent platinum furnaces P_1 and P_2 (see Fig. 1) were directed onto a tungsten filament H heated to temperature T. The positive and negative ions formed on the filament were analyzed by means of a magnetic-sector mass spectrometer. The molecular beams could be independently blocked by means of magnetically controlled shutters Z_1 and Z_2.

Fig. 1

Mass-spectrometric analysis showed that, during ionization of NaBr and Na_2S molecules, only Na^+ ions are observed in the spectrum of positive ions, while Br^- and S^- are observed in the spectrum of negative ions.

At equal densities of the NaBr and Na_2S molecular beams, the current of negative sulfur ions at all filament temperatures was two to three orders of magnitude smaller than the current of negative bromine ions, and in absolute value amounted to $\sim 10^{-15}$ A. To measure such small currents we used an ion-electron multiplier (M) of the box type with an open input, onto whose first dynode the ion beams fell after leaving the mass analyzer. The multiplier dynodes were made of a Cu–Be alloy and were only weakly activated by thermal treatment. Under these conditions the total multiplication coefficient in 12 stages was $\sim$ 2000, but it changed hardly at all with time and was very resistant to the action of atmospheric air. The electron current from the collector plate of the multiplier was fed to the input of an ordinary electrometric amplifier of the EMU-3 type. The minimum ionic current that could be reliably recorded with such a measuring device was $\sim 10^{-17}$ A.

The experimental procedure was as follows. Pure anhydrous Na_2S was prepared from the initial crystalline hydrate $Na_2S \cdot 9H_2O$ ([3]). The resulting Na_2S and chemically pure NaBr were placed in separate platinum furnaces and subjected to prolonged heating in a high vacuum

with a gradual increase of the temperature of the furnaces to values higher than the working ones. Before measurements of the currents of Br^- and S^-, the currents of positive sodium ions formed during ionization on the filament of, alternately, beams of NaBr and Na_2S were equalized. The additivity of the Na^+ currents during ionization of both beams (both shutters open) was also checked.

We assume that at tungsten temperatures above 1800°K complete dissociation of the salts Na_2S and NaBr occurs, and equality of the positive sodium currents therefore means that each second on the tungsten surface there are formed n_1 free bromine atoms and $n_2 = \frac{1}{2}n_1$ sulfur atoms, which are partially ionized in accordance with formula (1). In all measurements of the ratios of the currents $\frac{I_1}{I_2}$ (I_1 is the current of Br^- ions and I_2 is the current of S^- ions), the constancy of the density of the molecular beams of salts from the furnaces was periodically checked by measuring the corresponding Na^+ currents.

The temperature of the tungsten filament was determined with an optical pyrometer. Measuring the ratios of currents I_1/I_2 at different filament temperatures T, we calculated, by formula (4), the difference in the electron-affinity energies of bromine and sulfur atoms. Formula (4) also contains the statistical weights of bromine and sulfur in the atomic and ionic states. In the ground states the statistical weight of the bromine atom is $g_{a1} = 4$, and that of the negative bromine ion is $g_{p1} = 1$; for the sulfur atom $g_{a2} = 5$, and for the sulfur ion $g_{p2} = 4$. But the sulfur atom has two excited states, $^3p_1$ and $^3p_0$, close to the ground state; taking them into account, the statistical weight for it in the temperature range from 1800 to 2300°K should be taken as $g_{a2} = 8$. The excited states of bromine atoms at filament temperatures up to 2300°K may be disregarded, and for negative ions Br^- and S^- they are unknown. Therefore, in calculating the quantity $s_1 - s_2$ by formula (4), we took the ratio $\frac{A_1}{A_2} = 2$, allowing for the excited states of the sulfur atom.

From the experimentally measured ratios of currents I_1/I_2, values of the difference $s_1 - s_2$ were calculated for various temperatures of the tungsten filament in the interval from 1800 to 2300°K. The mean value from more than 80 independent determinations of the difference of the electron-affinity energies of bromine and sulfur atoms proved to be

$$s_1 - s_2 = 1.23 \pm 0.05 \text{ eV}.$$

The indicated error is the arithmetic mean error of all determinations. It is consistent with our estimate of the accuracy of measuring the ratio I_1/I_2 and the filament temperature.

However, possible differences in the coefficients of secondary ion-electron emission of Br^- and S^- ions on the first dynode of the multiplier and in the transmission coefficients of the mass spectrometer for these ions could have led to a systematic error in measuring the ratio of currents I_1/I_2. A specially performed experiment showed that these coefficients agree to within $\pm 20\%$ and, consequently, the systematic error in determining the difference $s_1 - s_2$ does not exceed 0.03 eV, while the total error is less than 0.1 eV.

The method we have used does not give absolute values of the electron-affinity energy. Therefore, if we take, as before ([2]), the electron-affinity energy of the bromine atom to be 3.6 eV, then the electron-affinity energy of sulfur atoms on the basis of our measurements will be $s_2 = 2.37$ eV. The accuracy of this quantity depends not only on the error in determining the difference $s_1 - s_2$, but also on how much the true value of s_1 for bromine atoms differs from the value adopted by us.

The value we have obtained for the electron-affinity energy of the sulfur atom agrees with the value $s_2 > 2.2$ eV found in experiments on the ionization of SO_2 molecules by electron impact ([4]). However, recently performed determi-

determination of the electron affinity energy of sulfur atoms by the method of photodetachment of electrons from negative ions S^- gave the value $s_2 = 2.07 \pm 0.07$ eV (5). The discrepancy of this value with that obtained by us may indicate that the electron affinity energy of bromine atoms is less than 3.6 eV, if, of course, both methods do not contain any unaccounted-for systematic errors.

Physical-Technical Institute
Academy of Sciences of the USSR

Received
23 IV 1957

CITED LITERATURE

1. I. N. Bakulina, N. I. Ionov, DAN, **99**, 1023 (1954).
2. I. N. Bakulina, N. I. Ionov, DAN, **105**, 680 (1955).
3. Yu. V. Karyakin, I. I. Angelov, *Pure Chemical Reagents*, 1955.
4. H. Neuert, *Ergebn. exakt. Naturwiss.*, **29**, 50 (1956).

5. L. M. Branscomb, S. J. Smith, *J. Chem. Phys.*, **25**, 598 (1956).

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