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Abstract

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ON THE ROLE OF CHEMICAL REACTIONS IN THERMIONIC EMISSION

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In mass spectrometry, natural and synthetic ion emitters are often used to obtain an ion beam; however, the phenomena that occur in this process have not been sufficiently studied. Apparently, the first attempt to investigate the mechanism of thermionic emission was the work of M. A. Eremeev et al. (^{1,2}). The authors, studying the influence of an electric field on the emission capacity of alkali ions from aluminosilicates, found that it is not consistent with the mobilities of the ions.

Later we reported (^{3}) on a study of the role of diffusion processes in the emission of cesium ions from aluminosilicates. We came to the conclusion that, in a thin emitter layer (less than 0.1 mm), diffusion at comparatively low temperatures (500—800°) and at significant concentrations is not the determining process. The present communication gives the results of a further study of the mechanism of thermionic emission: an investigation of the interaction of the emitter with a metallic substrate (heater). The emitter was an aluminosilicate ion exchanger of composition $Al_2O_3 \cdot 4SiO_2 \cdot xH_2O$, treated with a solution of cesium chloride. The work was carried out on an MS-4 mass spectrometer. It was found that, with a thoroughly purified platinum substrate, the emitter did not emit ions, whereas with a tantalum substrate a considerable ion current of Cs^+ was observed. If, however, when working with a platinum substrate, tantalum dust is preliminarily mixed into the emitter, an ion current appears of the same order as with a tantalum substrate.

A series of experiments was then carried out to study the dependence of the magnitude of the ion current on the chemical activity of the metal added to the emitter in the form of a powder. The substrate was a platinum ribbon washed with alcohol and water and calcined in the mass spectrometer until the alkali metals present in the platinum as impurities had completely "burned out." To measure the temperature, a platinum-platinum-rhodium thermocouple 0.1 mm in diameter was welded to the heater. The emitter mixed with the metal powder was applied to the middle part. At a temperature of about 500°, the appearance of a cesium ion current was observed. In all experiments, the work function was monitored from the temperature dependence of the emission current. The

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"activation energies" of Cs^+ emission proved, within the limits of experimental error, to be the same (2.70 ± 0.06 eV). The influence on the emission of Cs^+ of powders of the following metals was studied: copper, tungsten, tantalum, zirconium, and aluminum, as well as graphite powder. It turned out that, with increasing activity of the metal, the ion current increases. An admixture of graphite powder to the aluminosilicate emitter gave the same magnitude of emission current as tantalum.

It is evident that an interaction occurs between the emitter and the metal, leading to the formation of cesium atoms and, subsequently, to emission. Kunsman ([4]) had already indicated the possibility of this kind of interaction.

It should be noted that some platinum samples that had previously been used in operation (for example, subjected to calcination in the flame of a gas burner),

contain impurities (most often carbon), which may interact with the emitter and give a significant ion current. Carbonization of platinum was observed by us when working with graphite powder.

It was very interesting to check how the emitter on a platinum heater would behave at high temperature without additions of metal powders. Brief heating at 1500° led to the appearance of an intense Cs^+ current. When the temperature was lowered to the usual value ($\sim 600°$), the ion current became comparable in magnitude to the Cs^+ current obtained with a tantalum substrate. Undoubtedly, the emission upon lowering the temperature after such activation is due to products of thermal dissociation of the emitter.

Fig. 1. Dependence of the logarithm of the Cs^+ ion current at 655° on the quantity $-\Delta Z_1^0$.

It was also interesting to study the influence of an oxidizer on the emission. For this purpose a tantalum heater (substrate) with a welded platinum-platinum-rhodium thermocouple was used. First an emitter was placed on the substrate which, when heated, emitted Cs^+ ions (the ion current was $1.5 \cdot 10^{-11}$ A). After this control experiment the old emitter was removed from the substrate and a new one was placed, to which manganese dioxide (MnO_2) was added. Upon heating to the same temperature, a Cs^+ ion current was recorded that was 40 times smaller ($4 \cdot 10^{-13}$ A) than in the first case, the magnitude of the current gradually increasing with time, almost by a factor of 2.5 in 20 min (10^{-12} A). This experiment is yet another proof of the presence of chemical interaction in emission processes; the oxidizer shifts the equilibrium of the reduction reaction in the reverse direction, decreasing the concentration of cesium atoms. The subsequent increase in the current was evidently connected with depletion of the emitter layer in manganese dioxide.

To compare the results obtained, it was necessary to calculate the change in the isobaric-isothermal potential of the reaction

$$\mathrm{CsOR} + \frac{x}{y}\mathrm{Me} \rightleftarrows \mathrm{Cs} + \frac{1}{y} + \mathrm{Me}_x\mathrm{O}_y\mathrm{R},$$

where R is the aluminosilicate lattice. Such calculations could not be carried out because of the absence of thermodynamic constants for CsOR and R. But for reactions that differ from one another only in the chemical nature of Me and $\mathrm{Me}_x\mathrm{O}_y$, the values ΔZ_T^0 can be calculated to within a certain constant, and this difficulty can be avoided.

If ΔZ_T^0 is represented as

$$\Delta Z_T^0 = \Delta Z_{\mathrm{Cs}}^0 + \Delta Z_{\mathrm{R}}^0 + \frac{1}{y}\Delta Z_{\mathrm{Me}x\mathrm{O}_y}^0 - \Delta Z_{\mathrm{CsOR}}^0 - \frac{x}{y}\Delta Z_{\mathrm{Me}}^0,$$

then for all the reactions considered

$$\Delta Z_{\mathrm{Cs}}^0 + \Delta Z_{\mathrm{R}}^0 - \Delta Z_{\mathrm{CsOR}}^0 = \Delta Z_2^0$$

is a constant quantity.

Thus, the problem is substantially simplified and reduces to the calculation of

$$\Delta Z_1^0 = \frac{1}{y}\Delta Z_{\mathrm{Me}x\mathrm{O}_y}^0 - \frac{x}{y}\Delta Z_{\mathrm{Me}}^0.$$

The calculations of ΔZ_1^0 were carried out for the following processes:

$$\mathrm{Cu} \to \mathrm{Cu_2O}; \quad \mathrm{W} \to \mathrm{WO_2}; \quad \mathrm{Ta} \to \mathrm{Ta_2O_5}; \quad \mathrm{Al} \to \mathrm{Al_2O_3}; \quad \mathrm{Zr} \to \mathrm{ZrO_2}.$$

In the calculation, the values of the thermodynamic constants given in (5) were used.

Figure 1 shows the dependence of the logarithm of the ion current observed by us on the quantity $-\Delta Z_1^0$ at 655°. As can be seen, the logarithm of the ion current is a linear function of ΔZ_1^0; it follows from this that the magnitude of the ion current will depend linearly on the equilibrium constant of reactions of this kind, which confirms the existence of these reactions.

Thus, on the basis of the experimental material presented, it may be asserted that, at comparatively low temperatures, high cesium concentrations, and thin emitter layers, the factors determining the emission are the formation of cesium atoms as a result of a chemical reaction with the substrate and their ionization at the surface.

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