

**EXPERIMENTAL
STUDY OF THE
EXTERNAL
PHOTOELECTRIC
EFFECT FROM THE
SURFACE OF DILUTE
POTASSIUM
AMALGAMS IN THE
LIQUID AND SOLID
STATE**

![Fig. 1](figure)

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Fig. 1

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Abstract**Full Text****PHYSICAL CHEMISTRY****V. B. LAZAREV, Yu. I. MALOV****EXPERIMENTAL STUDY OF THE EXTERNAL PHOTOELECTRIC EFFECT FROM THE SURFACE OF DILUTE POTASSIUM AMALGAMS IN THE LIQUID AND SOLID STATE***(Presented by Academician I. I. Chernyaev, 5 X 1964)*

In studies devoted to the adsorption of impurities on a metallic surface, the magnitude of adsorption is usually calculated from data on the dependence of surface tension on concentration, using the well-known Gibbs formula ⁽¹⁾. In this way, adsorption can in principle be determined both on the surface of a melt and on the surface of the solid phase. In practice, however, methods for determining the surface tension of solids are not so reliable and theoretically rigorously substantiated as is the case for the liquid phase ^(2,3). Therefore, the dependence of the surface tension of solid solutions on the concentration of additives is often judged on the basis of experimental data pertaining to the molten state, assuming that substances which lower the surface tension of solutions in the liquid state possess analogous properties in the case of the solid phase ⁽³⁾.

Fig. 1

We measured the photoemission current from the surface of dilute potassium amalgams both in the molten and in the solid state, first, in order to establish whether impurities which in the liquid phase have the ability to increase their content in the surface layer as compared with the bulk do indeed retain this property in the solid phase, and, second, in order, by comparing data on the photoelectric properties of potassium amalgams with the data available in the literature on their surface tension, to draw a conclusion about the relation between these quantities.

Measurements of the photocurrent from the surface of potassium amalgams were carried out with an instrument constructed by us (Fig. 1). Before the start of the instrument was subjected to prolonged thermovacuum treatment; then

Fig. 2. Dependence of photocurrent from the surface of liquid amalgams on potassium concentration at 25° and wavelengths of incident light 3663 \AA (1) and 3132 \AA (2)

Figure 2: Fig. 2. Dependence of photocurrent from the surface of liquid amalgams on potassium concentration at 25° and wavelengths of incident light 3663 \AA (1) and 3132 \AA (2)

about 20 g of mercury of the highest purity grade (99.99999%) was distilled in vacuum into reservoir *1*, and a certain amount of potassium amalgam was poured into reservoir *2* from an ampoule broken under vacuum by means of a striker controlled by an electromagnet; after this the instrument was sealed off from the vacuum system along lines *I–I* and *II–II* and placed in front of the exit slit of the monochromator.

Monochromatic light, obtained from a PRK-2 mercury lamp by means of a ZMR-3 quartz monochromator, was directed onto the entrance window *3*, made of uviolet glass, and through an aperture in the anode *4* reached the surface of the amalgam *5*, connected to the cathode *6*, which in turn was connected to the input part of a dc measuring amplifier, from whose readings the quantities were measured directly. A constant potential difference between the anode and the cathode was produced by a battery of cells.

Fig. 2. Dependence of the photocurrent from the surface of liquid amalgams on potassium concentration at 25° and an incident-light wavelength of 3663 \AA (1) and 3132 \AA (2)

Tube *7* was connected to a Dewar filled with liquid nitrogen. A miniature resistance furnace was immersed in the latter, by means of which regulation of the flow of cold gaseous nitrogen was achieved; this nitrogen passed through the thermostated chamber *8* and cooled the amalgam to the required temperature. The temperature was measured by means of a platinum-gold-palladium thermocouple introduced through tube *9*. The outer glass vacuum jacket *10* protected the cooling agent from warming and the walls of the instrument from moisture condensation, which was important for avoiding leakage currents.

After completion of the measurements of photocurrents under illumination by different wavelengths and at different temperatures, the instrument was disconnected from the amplifier input and, rotating it about an axis perpendicular to the plane of the drawing through an angle somewhat less than 90° , clockwise and back, part of the amalgam was poured into the microburette *11*. Then, after measuring the amount of amalgam poured into *11*, several drops of amalgam were poured from *11* through capillary *12* into tube *13* and from there into reservoir *1*, rotating the instrument about the same axis through an angle less than 90° counterclockwise and back. Having then measured the amount of potassium amalgam remaining in microburette *11*, it was possible to calculate how much amalgam had passed into reservoir *1* and, knowing the amount of

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

mercury in it, to calculate the concentration of the resulting amalgam. The possibility of using a U-shaped microburette for preparing alloys was described in (5).

Some of the results obtained in studying the concentration dependences of the photocurrent from the surface of potassium amalgams are presented in Fig. 2, from which it is seen that the photocurrent magnitude increases sharply with increasing potassium content in the amalgams in the region of extremely low concentrations, and that this growth, although it slows down, continues subsequently as well (6).

Having determined, from the spectral characteristics obtained, the value of the red threshold of the photoelectric effect, we calculated the work function value electron from the surface of dilute potassium amalgams. Comparing it with the data of P. P. Pugachevich and O. A. Timofeevicheva⁵ on the surface tension of potassium amalgams (see Fig. 3), we consider it interesting to note the analogous course of the concentration dependences of these two physical quantities, which is apparently explained by one and the same cause determining both the change in surface tension and the work function—adsorption of potassium on the surface of mercury. It is not yet entirely clear how the experimental data on the steady increase of the photocurrent with increasing potassium concentration (Fig. 2) are reconciled with the results of adsorption calculations, which revealed the existence of sharp maxima on the adsorption isotherms^{5,7}.

Fig. 3. Concentration dependences of the electron work function (*a*) and the surface tension (*b*) of potassium amalgams

Fig. 4. Concentration dependences of the photocurrent from the surface of liquid (1) and solid (2) potassium amalgams at an incident-light wavelength of 3663 Å

With decreasing temperature an increase in the photocurrent and a shift of the “red limit” into the long-wavelength region were found, which may be explained by an increase in adsorption as the temperature decreases³.

The concentration dependences of the photocurrents from the surfaces of liquid and solid amalgams have an analogous character, as is seen from Fig. 4, which presents the dependences of the photocurrent from the surface of liquid amalgams at +25° and from the surface of solid amalgams at −40° on the potassium content. These data may be regarded as confirmation of the conclusion that

potassium is significantly adsorbed on the surface of mercury both in the liquid and in the solid state.

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