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Some Problems of Electrochemical Kinetics in the Light of Photoemission Studies

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It is shown on the basis of photoemission data that the electronic work function of a metal in solution is independent of the nature of the metal. The photoemission method for the measurement of the Ψ' potential yields results which agree with calculations based on the Gouy-Chapman theory. Measurements of photocurrents in acid solutions permit the experimental observation and investigation of non-activated electrochemical reactions of atomic hydrogen on various metals.
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INTRODUCTION

The specific features of photoelectron emission at the interface between metals and electrolyte solutions[1], whereby a distinction can be drawn between such emission and photoemission from metals into a vacuum, are associated primarily with the presence of the electrical double layer at the metal–solution interface, and also with the occurrence of homogeneous and heterogeneous reactions in the vicinity of the electrode. These are manifested in a series of general relations typical for the usual electrode processes. Therefore the study of the photoemission of electrons may be regarded as a new approach to the investigation of the fundamental problems of the electrical double layer structure and electrode kinetics. In this connection it is significant that photoemission constitutes the simplest form of electron transition at the interface which is not associated with adsorption and dissociation or formation of chemical bonds and it is therefore particularly convenient for investigations of this kind. Certain results of photoemission studies are discussed below, these are closely related to the fundamental problems of modern theoretical electrochemistry in the formulation and solution of which Frumkin's studies have been of decisive importance.

II. THE ELECTRONIC WORK FUNCTION OF THE METAL IN SOLUTION AND THE NATURE OF THE METAL

The photoemission of electrons from a metal into an electrolyte solution is a threshold phenomenon, like photoemission into a vacuum, the quantitative description of which is based on the concept of the electronic work function of the metal in the given medium. Owing to the presence of the electrical double layer, in which virtually the entire potential jump between the metal and the solution is concentrated, the electronic work function of the metal in solution w_{ms} depends on the electrode potential:

$$w_{ms} = w^0_{ms} + e\varphi, \qquad (1)$$

where w^0_{ms} is the work function of zero potential and e the absolute electronic charge. In photoemission Eqn. (1) is valid provided that the electrical double layer is completely transparent to the emitted electrons[2]. In contrast to emission into an electrolyte, for emission into a vacuum the electronic work function is almost independent of the potential difference applied from the outside (with the exception of special cases in autoelectron emission), since the resulting barrier due to the internal potential difference between the photocathode and anode extends throughout the space between the electrodes and is therefore impermeable to photoelectrons.

For this reason, the concepts of the electronic work function of the metal *in vacuo* and in an electrolyte are not physically equivalent. In the first system the electron work function is understood as the work of transferring the electron from the bulk of the metal into a vacuum to a distance where the Volta potential is constant (this distance is of the order of 10^{-5}–10^{-4} cm).[3] In the general case this work differs from the work of transferring the electron from the metal to infinity *in vacuo* (the electrochemical potential). In the second system the electronic work function is the work of transferring the electron from the metal to the bulk of the solution where there is no double layer field.

Metals at the same electrode potential are characterised by identical electronic work functions in solution, since in this case electron transfer from one metal to another does not require an expenditure of energy. Therefore Eqn. (1) is universal and independent of the nature of the metal.

The quantitative relation between the photocurrent j, on the one hand, and the energy of the light quantum $\hbar\omega$ and the electrode potential, on the other, is described by a 5/2 law[1]:

$$j = A(\hbar\omega - \hbar\omega_0 - e\varphi)^{5/2}, \qquad (2)$$

where $\hbar\omega_0 = w^0_{ms}$ and A is a constant which depends on the nature of the metal. Extrapolation of the experimental $j^{0,4}$–φ photocurrent curve on the basis of Eqn. (2) makes it possible to find the threshold potential φ_0 and hence the electron work function at $\varphi = 0$:

$$w^0_{ms} = \hbar\omega - e\varphi_0.$$

Experimental data obtained for different metals are presented in Fig. 1.[4] The zero-charge potentials of the test metals and hence their electronic work functions *in vacuo*

differ significantly (by up to 0.5 V). On the other hand, the threshold photoemission potentials are the same within the limits of experimental error.

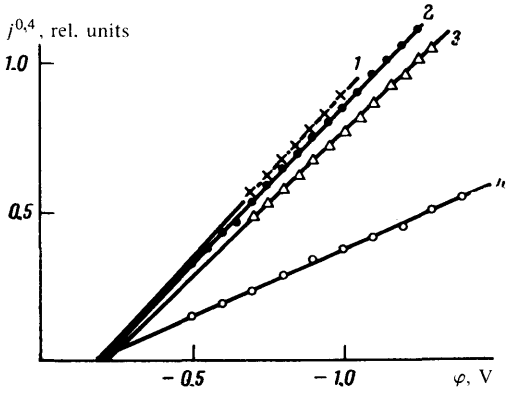


Figure 1. The constancy of the photoemission threshold: indium (0.1 *N* KF); *2*) bismuth (0.5 *N* KCl); *3*) lead .5 *N* Na_2SO_4); *4*) mercury (0.5 *N* KF); electron acceptor—O; light wavelength —365 nm; the potentials are quoted relative to the saturated calomel electrode throughout.

There exists a universal empirical relation (for aqueous solutions, potential measured relative to saturated calomel electrode) for the electronic work function w_{ms}, which is independent of the nature of the metal which determines φ_0:

$$w_{ms}(\varphi) = 3.45 + e\varphi. \qquad (3)$$

The conclusion that the electronic work function is independent of the nature of the metal agrees with the concepts developed for the first time by Frumkin[5,6], according to which the electronic work function *in vacuo* does not enter in an explicit form into the kinetic slow discharge equation when the potential is referred to a fixed reference electrode.

The constancy of the threshold potential is maintained also when the structure of the electrical double layer is altered (for example, on specific adsorption of various substances, which alter the zero-charge potential), since the double layer remains fairly thin and therefore transparent to the emitted electrons[7].

III. THE "ψ' CORRECTION" IN PHOTOEMISSION AND THE POSSIBILITY OF A DIRECT EXPERIMENTAL DETERMINATION OF THE ψ' POTENTIAL

The kinetics of electrode reactions were considered for the first time in Frumkin's studies[8] in relation to the electrical double layer structure. In the simplest but fairly general case the influence of the double layer on the rate of the electrode reaction is taken into account quantitatively by introducing the ψ' potential into the equation for the slow discharge current. In photoemission the role of the double layer is in many ways similar to its role in electrochemical kinetics. Whereas in concentrated electrolyte solutions the double layer is almost transparent to photoelectrons, in dilute solutions its diffuse component is no longer transparent to such electrons, since its thickness may exceed (for electrolyte concentrations smaller than 0.1 *N*) the de Broglie wavelength of the emitted electrons. In this case the electronic work function changes (relative to the value for the concentrated solution) by an amount $e\psi'$ and the photoemission equation (2) becomes[1]:

$$j = A[\hbar\omega - \hbar\omega_0 - e(\varphi - \Psi')]^{3/2}. \qquad (4)$$

It follows from Eqn. (4) that the rate of photoemission is not influenced by the total φ potential jump, but only by its component $\varphi - \psi'$. The complete analogy with the influence of the ψ' potential on the activation energy for the discharge of the species in the outer Helmholtz plane of the electrical double layer is striking.

The possibility, in principle, of an experimental determination of the ψ' potential follows from a comparison of the emission photocurrents in dilute [Eqn. (4)] and concentrated [Eqn. (2)] solutions. †

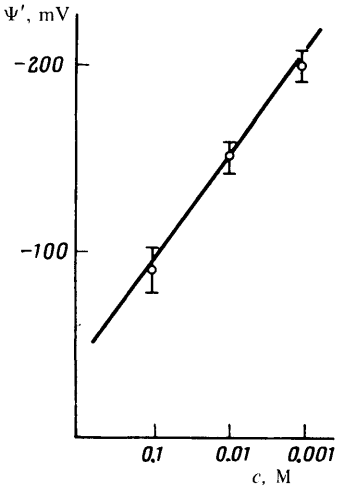


Figure 2. Variation of the ψ' potential with the concentration of the electrolyte (HCl); mercury electrode, -1.1 V; continuous straight line —calculation based on the Gouy–Chapman theory.

The photocurrents for mercury and lead electrodes have been measured[9] in HCl solutions at different concentrations (from 0.001 to 1 *N*) and negative potentials where $\psi' < 0$. The ψ' potentials found from the shift of the $j^{0,4} - \varphi$ curves in dilute acid solutions along the potential axis relative to the curve in 1 M HCl are presented in Fig. 2 as a function

† In general, difficulties arise in such measurements; these are associated with the influence of the structure of the double layer not only on the emission step itself, which is described by Eqns. (2) and (4), but also on the processes accompanying emission. These processes are mainly migration of hydrated electrons in the field of the diffuse layer. To eliminate undesirable effects of this kind, which complicate the determination of the ψ' potential, it is necessary to create conditions where hydrated electrons hardly return to the electrode and therefore the influence of the structure of the double layer reduces merely to a change in the emission current itself. In the measurements described below this condition was fulfilled.

of the logarithm of the concentration of the electrolyte. The continuous straight line was calculated on the basis of the Gouy–Chapman theory. The quantitative agreement between the experimental and theoretical data is of fundamental importance, since the photoemission method for the determination of the ψ' potential and the traditional differential capacitance method are based on completely different physical approaches. It must be emphasised that in the Gouy–Chapman theory one considers the ψ' potential averaged over a plane parallel to the electrode surface and not the local ψ' potential which can be determined, in principle, from kinetic measurements. By virtue of the delocalisation of the emitted electron in this plane, the averaged ψ' potential is also measured by the photoemission method. Therefore the above comparison of the theory with experiment is physically justified.

IV. THE OBSERVATION AND INVESTIGATION OF ELECTRODE REACTIONS WITHOUT ACTIVATION ENERGY

Electrode reactions differ from the usual chemical reactions specifically by the fact that their activation energies increase linearly with electrode potential. On the basis of the Brønsted relation, Frumkin et al.[10] concluded that at high overvoltages the activation energy for the electrode process can become zero and the rate of reaction can cease to depend on the potential. Such non-activated electrode reactions could not be detected until recently by the usual electrochemical methods because the direct measurement of the limiting currents for non-activated discharge was precluded by diffusion-dependent restrictions, which inevitably arose. Only recently was a system discovered[11] in which the supply of the reactant to the surface did not constitute the rate-determining step and the measured limiting current could be treated as the current of a process without activation energy ‡.

Electrode reactions without activation energy were observed for the first time (although not by direct measurement of the limiting current) in a study of the photoemission of electrons from mercury in acid solutions[13]. As a result of the capture of hydrated electrons by the hydronium ions in the layer of solution adjoining the electrode, hydrogen atoms are formed and then removed from the electrode surface via two electrochemical reactions:

$$H + H_2O\,(H_3O^+) + e^- \rightarrow H_2 + OH^-\,(H_2O); \quad (5)$$

$$H + H_2O \rightarrow H_3O^+ + e^-. \quad (6)$$

The measurement of the photocurrent in such systems and in systems where there is no oxidation of atomic oxygen makes it possible to determine the ratio of the currents consumed in the oxidation and reduction of hydrogen atoms. Analysis of the kinetic scheme showed that this ratio is $(2j_0 - j)j$, where $2j_0$ is the photocurrent in the absence of the oxidation of hydrogen and j is the measured photocurrent. The variation of $(2j_0 - j)/j$ with φ is described by the equation[13]

$$\varphi = \frac{2.3\,RT}{(\alpha + \beta)\,F}\left(\lg\frac{2j_0 - j}{j} + \text{const}\right), \quad (7)$$

‡ Krishtalik's observation[12] of barrier-free hydrogen ion discharge processes served as direct evidence for the occurrence of non-activated ionisation of hydrogen on mercury.

from which it is possible to determine the sum of the transfer coefficients $(\alpha + \beta)$ for the two coupled reactions (5) and (6).

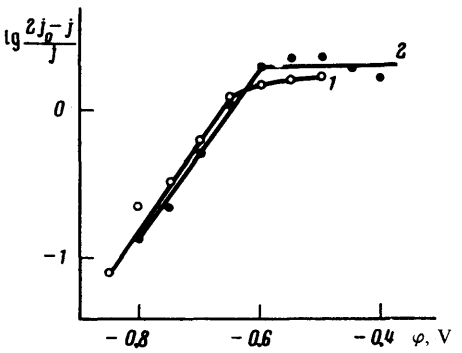


Figure 3. Determination of the transfer coefficients for the reactions of atomic hydrogen on bismuth by Eqn. (7): *1*) 0.5 *N* KBr + 0.003 *N* HCl; *2*) 0.5 *N* KCl + 0.06 *N* HCl.

As an example, Fig. 3 illustrates the graphical treatment in terms of Eqn. (7) of experimental data obtained for a bismuth electrode[4]. At potentials more positive than -0.6 V the ratio of the atomic hydrogen oxidation and reduction currents is independent of φ and, when $\varphi < -0.6$ V, the ratio decreases with the potential. Accordingly, $\alpha + \beta = 0$ in the region of positive potentials and $\alpha + \beta = 0.4$ in the region of negative potentials. The sum of the transfer coefficients being equal to zero is equivalent to each being zero. Thus reactions (5) and (6) both proceed without activation energy when $\varphi > -0.6$ V. The electrochemical desorption reaction (5), being a cathodic reaction, remains without activation energy (i.e. $\alpha = 0$) also at negative potentials when $\alpha + \beta = 0.4$. Hence it follows immediately that the transfer coefficient for the hydrogen ionisation reaction $\beta = 0.4$. This value agrees with the results of direct measurements of the rate of discharge of the H_3O^+ ion on bismuth[14], for which the transfer coefficient $1-\beta = 0.6$; this also demonstrates the overall self-consistency of the process mechanism described. The electrochemical desorption reaction (5) on bismuth proceeds mainly with participation of water molecules, in agreement with the hypothesis that the process mechanism involves zero activation energy[15].

Reactions with zero activation energy involving atomic hydrogen have also been observed on mercury[13] and antimony[16]. The kinetics of these processes are sensitive to the adsorption on the electrode of various substances which alter the structure of the double layer and may be formally interpreted[4] on the basis of Frumkin's theory of the ψ' effect.

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