FUNDAMENTALS OF THE THEORY OF ELECTRODE PHOTOEFFECT

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In this paper we consider the specific regularities governing the surface photoeffect on the metal/solution boundary (electrode photoeffect). During photo emission into an electrolyte solution or a polar dilectric the surface forces decline rapidly with distance. Applying this general premise alone in a single-photon approximation for the photocurrent one at the limit of a degenerate electron gas, we get the following equation:

$$I \sim (\omega - \omega_0)^{5/2}, \tag{1}$$

(ω_0 is the red photoeffect boundary, ω the radiation frequency), i.e., "the five-halves law" as distinct from $I \sim (\omega - \omega_0)^2$ according to Fowler's well known theory for photoemission into a vacuum. During polarization of the electrode the red boundary of the photoeffect shifts:

$$\hbar\omega_0(\varphi) = \hbar\omega_0(0) + e\varphi, \tag{2}$$

where $\omega_0(0)$ is the red boundary when there is no polarization. Equations (1)-(2) determine the volt-ampere characteristic of the contact under electrode photoeffect conditions. Comparison of theory and experiment shows a good quantitative accordance. From the experimental data we can approximately calculate the work function of the fast electrons from mercury into water W = 3.3 eV (for vacuum W = 4.5 eV). We discuss the general nature of the dependence of photocurrent on frequency, including the region further away from the threshold, and also the dependence of the electrode photoeffect on radiation polarization.

The creation of a current in electrochemical systems when one of the electrodes is illuminated was first detected in 1839 and was known as the Becquerel effect [1] after its discoverer. Later studies [2-4] showed that this phenomenon may be due to several factors different in principle. For example, light may be absorbed by dissolved matter, as a result of which homogeneous photochemical reactions begin in the body. In this case the electrode proper does not take part in the photoprocess and only reacts to changes occurring deep in the solution. Over the last few years there has been intensive experimental investigation of effects occurring when a mercury drop electrode is irradiated by visible light or neighboring ultraviolet light under conditions where the processes occurring on the surface are the determining ones [5-9].

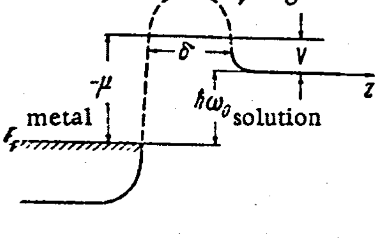

Fig. 1. Metal/solution interface under electrode photoeffect conditions. Surface potential barrier, the true value of which is unknown, is shown by the dotted line.

Several different mechanisms have been put forward to explain the photocurrent, which may not only be cathodic, but also anodic. According to Heyrovsky [5], the observed photocurrent is due to the formation of a complex with charge transport on the surface. Molecules or ions from the solution close to the surface of the mercury electrode, according to Heyrovsky, may create a higher or lower electron concentration there. Due to the action of light this complex may be destroyed and the molecule or ion may leave the surface. As a result the charge that was previously "pulled" towards the surface enters the body of the electrode, and this is what is recorded in the form of a photocurrent. Depending on the

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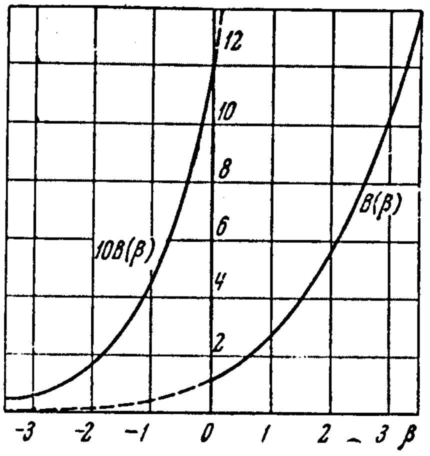

Fig. 2

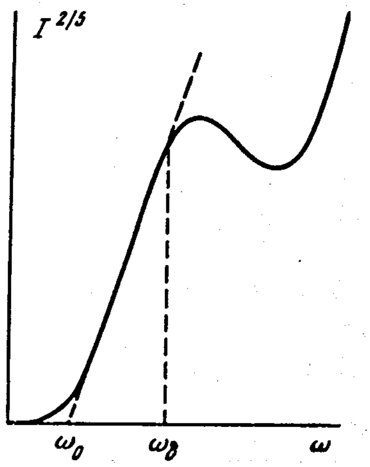

Fig. 3

Fig. 2. Graph showing functions B(β). In region $-3.5 < \beta < 0$ the curve $10B(\beta)$ can be used to obtain greater accuracy.

Fig. 3. Schematic view of relationship between photocurrent to the power of $^2/_5$ and light frequency ω; ω_0 is the threshold frequency; ω_δ is characteristic frequency associated with the width of the surface potential barrier.

properties of the molecule or ion complexes formed, the photocurrent created in this way may either be positive or negative.

According to Berg [8], the electrochemical reactions on the electrode surface are speeded up by the light. Here the photocurrent is regarded as the difference between the current under conditions of illumination and the dark current. The light "further excites" the electrons in such a way that the probability of their transition to molecules or ions in the solution (and back again) becomes substantially greater than when there is no illumination.

Finally, Barker [6] has pointed out that a substantial part in this effect must be played by the external photoeffect, i.e., transition of electrons that have absorbed light quanta from the solid to the surrounding medium; this point of view has latterly been developed in other communications [7, 9, 21].

Thus, the effects occurring on the electrode when irradiated by light (Heyrovsky suggests the term "electrochemical photoeffect" to sum them up) may be divided into two groups. The first group of effects is associated directly with the photoemission of electrons from a metal into the electrolyte solution; the second group is not directly associated with the photoeffect proper, but is determined by the photochemical reactions occurring on the electrode and phenomena of the type of complex formation with charge transport.

In view of the great difference in regularities governing photoemission from metal into electrolyte solution and those governing photoemission in a vacuum* we will call the external photoeffect from metal to electrolyte solution by a special term—the electrode photoeffect or electrode photoemission.

Here we will consider the fundamental regularities governing the electrode photoeffect (electrode photoemission) when there are no photochemical reactions on the electrode or formations of the complex type with charge transport, which happens in any case when the energy of the emitted electrons exceeds several tens of eV. The calculation used below may also be applied for a quantitative description of a photocurrent under conditions where the above-mentioned complexes are formed, but this will be dealt with in a separate publication.

We should stress that due to the specific features of the metal/electrolyte interface structure, by applying a comparatively small external potential to them we can vary the emission properties of the electrode to a very substantial degree. This is one of the reasons for the fact that the study of electrode photoeffect is of great interest both for the theory of surface effects as well as in connection with practical applications of the photoemission.

At light frequencies below the frequency of so-called ultraviolet translucence of metal [12], electron photoemission stems basically from a very narrow near-surface layer of metal, with the absorption of photons becoming

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*As will be demonstrated below, Fowler's theory [11,12] for photoemission from metal in a vacuum is applicable in the given case, despite the assumptions in [7].

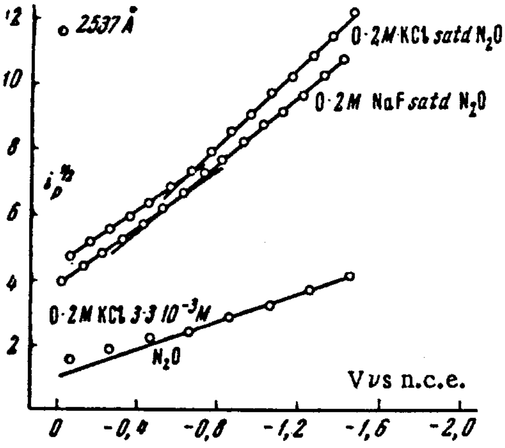

Fig. 4

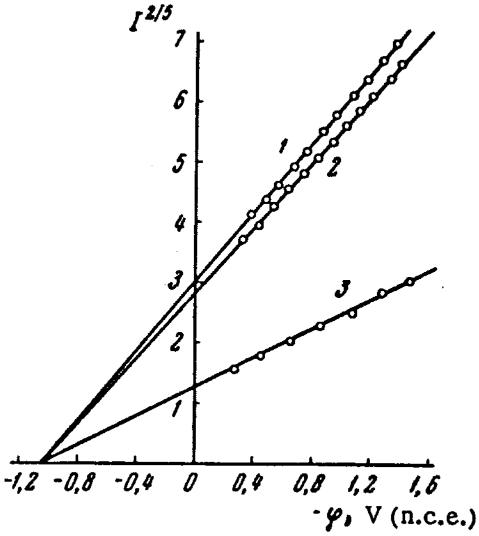

Fig. 5

Fig. 4. Results of experiments conducted by Barker and coworkers (from [7]). The square of photoeffect i_p (in referred units) as a function of the potential V in volts reckoned from the normal calomel electrode.

Fig. 5. Processing of Barker's results [7] using Eqs. (10b) and (12). Photocurrent I to the power of $^2/_5$ (in referred units) as a function of the electrode potential with the reverse sign (in volts). As zero we take the potential of a normal calomel electrode. Wavelength of light 2537 Å. Composition of solution: 1) 0.2 M KCl, saturated N_2O; 2) 0.2M NaF, saturated N_2O; 3) 0.2 M KCl, $3.3 \cdot 10^{-3}$M N_2O.

possible through interaction between electrons and the potential barrier on the interface.* As the frequency further grows and ultraviolet translucence approaches, the electrons begin to fly out of the metal body as a result of participation in the photon and electron interaction either by crystal lattice oscillations, or impurity atom oscillations (external body photoeffect). The magnitude of the photocurrent in this case rises sharply. In the region of frequencies corresponding to ultraviolet translucence, purely surface effects now play a secondary role. Clearly, in the study of physiochemical processes on the phase interface of greatest interest is the region of light frequencies corresponding to the surface photoeffect (on the energy scale $\hbar\omega \approx 1$ to 10 eV).

When considering photoemission effects on the interface, processes involving photoelectrons may be grouped into three successive stages: 1. electron photoemission proper, i.e., the transition of electrons absorbing light quanta through the interphase; 2. retardation of electrons in the liquid due to their transmission of energy to solvent molecules (the retardation usually occurs at distances of tens and hundreds of angstrom units from the surface; i.e., beyond the reach of surface forces); 3. solvation of "heat electrons and subsequent physiochemical transformation (diffusion, capture by acceptors and "traps", chemical reactions in the body, on the electrode, and so forth).†

Here we will limit ourselves to considering only the photoeffect proper, and not deal with the problem of further behavior by the emitted electrons in the liquid. Experimentally observed current I_{ex} in electrolyte solutions should, however, be proportional to the photoemission current I.‡

Let us proceed from the following natural assumptions: 1) the field of the outside electromagnetic wave is much smaller than the molecular fields. Since the latter are extremely large (of the order of 10^8V/cm), this condition is always valid, even for a laser ray with a field intensity of the order of 10^6 V/cm; 2) we can disregard the disruption of thermodynamic equilibrium for electrons inside a solid during the passage of a photoelectric current. This condition is practically always the case; 3) we can disregard the effect on the movement of electrons of the magnetic field from the incident wave, which is equivalent to disregarding the relativistic effects. When considering the quanta energy this is also possible in all cases.

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*A "free" electron cannot absorb a photon at all by virtue of the laws of conservation of energy and impulse.

†Generally speaking, isolation of stages II and III is to some extent conditional; for example, retardation may be accompanied by chemical reactions.

‡Deviations from linearity may occur if the concentration of photoelectrons in the liquid is so strong that the body charge created by it becomes substantial. Here the evaluations may be made in the same way and when considering the effect of the body charge on photoemission in a vacuum [11].

Under these conditions the general expression foı the photo-emission current from the metal, without dependence on the model, can be written down in the form

$$I=\int j(E,\mathbf{p}_p\mathbf{A})F(E,\mu)\rho(E,\mathbf{p}_p)\,dE\,d\mathbf{p}_p. \tag{1}$$

Here A is the vector potential of the electromagnetic wave, E and $p_p = \{p_x, p_y\}$ are, respectively, the initial energy and pulse components directed parallel to the surface of the electrons in the metal; $F(E,\mu)$ is a Fermi distribution function with chemical potential μ; j is the asymptotic (i.e., at $z\rightarrow\infty$) value of the current density, averaged over the metal surface (Fig. 1), and ρ is the distribution density function. Integration is made over the whole of the phase space. To find j in each specific case we have to solve the complex quantum-mechanical problem of determining the dependence of j on the properties of the interface. However, a number of important conclusions may be drawn at this point from (1) and also from general considerations on the structure of the equation for current density.

Calculation of Electrode Photoeffect

Most of the electrons flying into the liquid possess energy in the given case that considerably exceeds kT, and their motion can be described as the motion of particles with an effective mass m in an average potential cavity, the depth of which V is a function of the properties of the liquid (in the case of emission in a vacuum V = 0 and m is equal to the electron mass m_e). In this respect the motion of "hot" electrons in polar liquids does not differ from motion in polar crystals [14]. Limiting ourselves for the moment to considering processes that involve absorption of only one photon,* we get $E+\hbar\omega=-V+(1/2m)(p_x^2+p_y^2+p^2)$ from the law of conservation of energy and pulse. Here p is the asymptotic value of the z component of the emitted electron pulse, i.e., p is unaffected by surface forces. The quantities p_x and p_y during transition through the interphase boundary remain equal to their previous value, since the potential barrier only exists along the z coordinate, hence $p_x^2+p_y^2=p_p^2$. Thus for p we get

$$p=\sqrt{2m(E+V+\hbar\omega)-p_p^2}. \tag{2}$$

From the general form of the quantum-mechanical operator for the current density [14] it follows that the asymptotic expression for j should take the following form:

$$j=e(p/m)\,|\psi_f|^2\theta(p^2). \tag{3}$$

Here ψ_f is the asymptotic value of the electron wave function of the electron that absorbed the quantum, so that the energy corresponding to ψ_f is $E+\hbar\omega$ (until the field was included the electron was described as a wave function of the initial state ψ_0 with energy E). The quantity $\theta(p^2)$ is the so-called θ function, given by the conditions

$$\theta(x)=\begin{cases}0 & \text{at } x\leqslant 0\\ 1 & \text{at } x>0\end{cases}.$$

The presence of a θ function in (3) shows that only those electrons whose pulse is purely material can make a contribution to the current. With respect to the function $|\psi_f|^2$, in a case in which there are no residence energy levels on the surface, we can assert the following. First, it is smooth in the integration area, which is limited by the presence of the θ function in (3). Second, $|\psi_f|^2$ at $p\rightarrow 0$ behaves as a constant, provided the surface potential fades fairly quickly. The problem of the behavior of function $|\psi_f|^2$ at $p\rightarrow 0$ has been considered in connection with solving problems of nuclear photoeffects [15]. Evaluations similar to those made for threshold sections of photogeneration [14, 15] show that $|\psi_f|^2$ can in any case be considered constant at photon energies $\hbar\omega$ corresponding to the final kinetic energy of electrons less than $\hbar^2/(2m\delta^2)$, where δ is the characteristic length of decline of the surface forces.† In other words, the de Broglie wavelength of the immediate electron should be greater than the width of the surface barrier. Evaluation shows that for the case in point this region of finite energies comprises in order of magnitude several electron volts, i.e., most of the energy region corresponding to the surface photoeffect.

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*Here the quantity serves as the smallness parameter $e^2/\hbar c = 1/137$.

†Strictly speaking, it is also necessary for the energy of the emitted electron to be less than E_F—the Fermi energy—reckoned from the bottom of the conductivity zone. Normally, however, this condition is weaker than the one mentioned in the text.

We should point out that during emission in a vacuum (or a dielectric with dielectric permeability close to one) the situation differs sharply from the one considered: there a substantial part is played by the image forces which have a long range. On account of this, for fairly low energies $|\psi_f|^2 \sim p^{-1}$ (and not const!), which justifies substitution of the constant at $p^2 > 0$ and zero at $p^2 < 0$ into (1) instead of (3), as is done in Fowler's theory [10, 11] for photoemission in a vacuum. In the case in point the substitution of (2) and (3) into (1) gives us

$$I = \frac{e}{m} \int_{-\hbar\omega - V}^{\infty} dEF(E, \mu) \int_{0}^{\sqrt{m(E+V+\hbar\omega)}} p\,|\psi_f|^2 \rho(E, \mathbf{p}_p)\, 2\pi\, |\mathbf{p}_p|\, d\,|\mathbf{p}_p|. \tag{4}$$

Taking it into account that by virtue of what has been said above, the quantity $|\psi_f|^2\rho$ in the integration region is a poor function of E and $\mathbf{p}_p$, we can take away the integral sign, after which integration with respect to $d|\mathbf{p}_p|$ is made directly. As a result we get

$$I = \frac{2\pi e}{3m} \overline{|\psi_f|^2 \rho} \int_{-\hbar\omega - V}^{\infty} \frac{dE}{e^{E-\mu/kT} + 1} [2m(E + V + \hbar\omega)]^{3/2}. \tag{5}$$

Here $\overline{|\psi_f|^2\rho}$ is the function $|\psi_f|^2\rho$ at a middle point.

The threshold frequency of a single photon photoeffect (red boundary) is determined by the condition $\hbar\omega_0 = W$, where W is the electron work function from a Fermi surface for metal in liquid; in the case under consideration $W = -(\mu + V)$ so that

$$\hbar\omega_0 = -(\mu + V). \tag{6}$$

substituting the variables $x = (h\omega + E + V)/(kT)$ in (5) and applying (6) we can rewrite the expression for I in the form

$$I = A_0 \left(\frac{kT}{\hbar\omega_0}\right)^{1/2} T^2 \chi B(\beta). \tag{7}$$

Here A_0 is the Sommerfeldt constant, equal to $A_0 = 4\pi e k^2 m_e/(2\pi h)^3 = 120\ \mathrm{a \cdot cm^{-2} \cdot deg^{-2}}$, χ is a dimensionless function determined by the properties of the metal and interface, and not dependent explicitly on T, and $\beta = h(\omega - \omega_0)/kT$. The universal function $B(\beta)$ in (5) is determined by the equality

$$B(\beta) = \int_0^{\infty} \frac{x^{3/2}}{e^{x-\beta} + 1} dx. \tag{8}$$

Thus, the fundamental regularities governing photoemission in the near-threshold frequency region, comprising several electron volts, is determined by the behavior of the universal function $B(\beta)$. We should stress that we have not made any assumptions either with regard to the shape of the potential barrier (apart from its rapid decline), or with respect to the properties of the Fermi surface of the metal (as distinct from in [10, 11, 18], where the model of free electron is freely used and an assumption is made with regard to the rectangular shape of the potential barrier). The function $B(\beta)$ was studied earlier [16] in connection with another problem – calculation of the mean electron gas energy. $B(\beta)$ can be described approximately by the equations

$$B(\beta) \approx 1.33\, e^{\beta} \quad \text{at} \quad |\beta| \gg 1,\ \beta < 0, \tag{9a}$$

$$B(\beta) = \frac{2\beta^{5/2}}{5}(1 + 5\pi^2/8\beta^2) \quad \text{at} \quad \beta \gg 1, \tag{9b}$$

with the error beyond the interval (−4; 4) being now less than 1%. Within the interval mentioned $B(\beta)$ may be determined by means of the graph shown (Fig. 2).

At T = 0 we get from (5), (7), and (9)

$$I = 0 \quad \text{at} \quad \omega \leqslant \omega_0, \tag{10a}$$

$$I = A_0 \chi \frac{2\hbar^2}{5k^2 \omega_0^{1/2}} (\omega - \omega_0)^{5/2} \quad \text{at} \quad \omega \geqslant \omega_0. \tag{10b}$$

As follows from (10), at $T = 0$ the formally introduced quantity ω_0 really is the red boundary of the external photoeffect. Variation in current with frequency close to the threshold can be described, according to (10b), by the "law of five over two." At $T \neq 0$ the concept of the red boundary becomes approximate, since in this case these is also a photocurrent at $\omega < \omega_0$. This is because at $T > 0$ on account of thermal excitations in the metal there are definitely electrons present with energies greater than the Fermi energy. It is these that contribute to the photocurrent at $\omega < \omega_0$ as well. The number of such thermal electrons in the metal, according to Boltzmann distribution, declines exponentially as their energy increases (the thermal "tail" of the Fermi distribution coincides with the Boltzmann distribution); in accordance with this, the photo current in the frequency region above the threshold $h(\omega_0 - \omega)/kT > 1$ should also decline exponentially with a drop in ω which accords with (9a). The dependence on temperature in this region also basically is determined by the exponential factor in (7) according to (9a). As the frequency increases and ω becomes greater than ω_0, the functional dependence on temperature rapidly vanishes and as we see from (9b), at $h(\omega - \omega_0)/kT \gg 1$ the photo current is again described by (10b), as in the case $T = 0$. It follows from this, in particular, that the quantity ω_0 may be determined from measurements made at $T \neq 0$ as well.

Let us consider another frequency dependence of the photocurrent at photon energies that are so high that $|\psi_f|^2$ can no longer be considered constant. It can be demonstrated that for fairly large p the corresponding ψ_f is the p Fourier component of a limited quadratic-integrable function. Hence, by virtue of the Riemann-Lebecq theorem on the properties of Fourier transforms [17], it follows that $|\psi_f|^2$ will decrease when p increases (with $|\psi_f|^2 \to 0$ at $p \to \infty$). This means that as p rises, the deviation from the "law of five over two" should incline towards a reduction in I.* By knowing the kinetic energy of the electrons at the "departure point" (corresponding to the frequency ω_0) we can determine the length of the range of the surface forces δ from the relationship

$$\hbar(\omega_\delta - \omega_0) = \hbar^2 / 2(m\delta^2). \tag{11}$$

As the frequency further rises, the drop in surface photoemission, however, may be overlapped by the incipient body photoeffect. The total dependence $I^{2}/_{5}(\omega)$ should therefore be described by a curve with a maximum (or maxima). The shape of this curve is shown schematically in Fig. 3. Let us stress that as distinct from the relationship given by Fowler's theory, the factor $\omega - \omega_0$ is present in (10b) to the power $^5/_2$, and not as a square,† since we have taken into account the further decrease in current density at $\omega \to \omega_0$. The physical meaning of this decrease is clear: At $\omega \to \omega_0$ the velocity of the escaping electrons p/m tends to zero, thereby decreasing the photo current density in proportion to p/m. In accordance with this effect, the temperature dependence in the frequency region above the threshold should also be slightly different in nature than in the theory [10].

Application of the potential difference φ between the metal and solution of electrolyte (electrode polarization) results in change in the depth of the potential cavity V by the quantity $e\varphi$. Correspondingly, according to (6) the red boundary of the photoeffect should also be shifted:

$$\hbar\omega_0(\varphi) = \hbar\omega_0(0) + e\varphi. \tag{12}$$

Here $\omega_0(0)$ is the threshold frequency when there is no further polarization of the electrode φ. The relationships found for I when (12) is taken into account determine the volt-ampere characteristic of the system metal/electrolyte under electrode photoeffect conditions on the assumption that we can disregard the influence of the variation in the electron density of the metal.

As follows from the properties of symmetry, it is only the z component of the electric field $\mathcal{E}_z$ that can bring about the quantum transition under consideration. This means that in the first order of the theory of disturbances, $\psi_f \sim \mathcal{E}_z$ and for the quantity χ we get $\chi \sim \mathcal{E}_z^2$. Thus, the photoemission current caused by polarized light is

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*It is assumed that there are no resonance energy levels.

†We should point out that the "law of five over two" was also derived in [18] for a particular model of an ideal electron gas at $T = 0$ in a rectilinear potential box. But the author's calculations [18] are unsuitable for the case in point of photoemission in a vacuum, since there always arise long-range image forces in this case.

proportional, apart from its dependence upon the angle of incidence, to the square of the sine of the angle between the plane of polarization and the plane of incidence (s-wave) [19] should bring about an extremely small effect. Dependence on polarization of radiation was experimentally observed during photoemission in a vacuum [20]. We should stress that experimental observation of strong dependence between photocurrent and light polarization points unambiguously to the presence of a surface photoeffect, since the other mechanisms that might be suggested to explain the photocurrent in physiochemical systems ought not to produce this kind of dependence. By employing sources with polarized light in the experiments we can hope to separate the surface and body components of the photoeffect at relatively high energies. In particular, we can in this way attempt to determine δ for those cases in which the body and surface photoeffects overlap even before the maximum is produced on the curve $I^{2/5}(\omega)$ (see Fig. 3).

Experimental Corollaries of the Theory

A controversial dependence between the photocurrent I and φ [21] has been derived in a whole number of experimental projects [7, 9]. In Fig. 4, which is taken from [7], we show data derived during a study of the surface photoeffect on mercury. The authors attempted to explain the results obtained by means of a quadratic dependence of the current on potential, following from Fowler's theory. As can be seen from Fig. 4, they were not successful since the experimental points corresponding to the fixed frequency and composition of the solution do not even lie on a straight line, which compels us to plot a graph with a bend that is not to be satisfactorily explained.

As an illustration of the developed theory, these experimental data are processed by means of Eqs. (10b) and (12). The results are shown in Fig. 5. We arrive at a family of lines proceeding from one point in close accordance with the theory for a fixed light frequency ($\lambda = 2537$ Å) and for different weak solutions. By knowing the potential of the intersection point and the wavelength of the radiation, we can use Eq. (12) to determine the work function for fast electrons from mercury to water at the zero charge potential. This quantity is approximately $W_{H_2O} = 3.3$ eV. The difference between this quantity and the work function in a vacuum ($W_{vac} = 4.5$ eV) characterizes the interaction energy between the superthermal electron and water. Correspondence with the theory is also found when processing other experimental data [9].

Let us stress that the use of Eqs. (10b) and (12) demonstrated above represents a new method of experimentally determining the work function which differs from the isothermal and isochoric methods that have been used so far [11], whereby the frequency of radiation and metal temperature are varied correspondingly. In the suggested method, which may be termed the method of variation in electrode potential, measurements are made at fixed temperatures and with the use of only one radiation frequency. If the work function is known, we may use the potential variation method to determine the zero charge point. From the variation in work function (or shift of the zero charge point) when substances adsorbed on the electrode are added to the solution we may gain an idea of the magnitude of the additional potential jump.

As follows from Eqs. (10b) and (12), the radiation frequency and electrode potential may be varied at the same time in such a way that $\omega_0(\varphi) - \omega$ remains constant. The explicit dependence between photo current I and frequency observed under these conditions is associated with the variation in function $\chi(\omega)$ (for a fixed solution composition). Experimental determination of this relationship may provide a direct possibility of finding a law for the attenuation of light on a metal surface.* This, in turn, opens the way for derivation of the path of the electron density on the metal/solution interface, i.e., to a fundamental characteristic of the surface on which, in the long run, all the physicochemical processes occurring on the interface depend.

Study of the electrode photoeffect in the vicinity of the threshold frequency where instead of a simple "five-halves law" we have to apply Eq. (7) and where an important part is now played by variation in energy by values of the order of kT, may provide valuable information on the structure of liquids in the near-surface layer, the role of thermal fluctuations in the solvent, the solvation rate of electrons, and so on.

Let us note a very special reason for possible deviation from the laws given at frequencies lying even further within the threshold region. Apart from the structural and thermal factors mentioned above, which play a part at $|\omega - \omega_0| \sim kT$, another reason for the deviation may be the occurrance of resonance surface electron levels. These levels, which may be associated with the formation of complexes with charge transport or other forms of chemical bonding on the metal surface may play a determining role when $\omega - \omega_0$ is close to the resonance value, normally of the order of tenths of an electron volt.

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*A detailed theoretical analysis shows that the dependence $\chi(\omega)$ should lie between $\chi \sim \omega^{-4}$ (the absence of marked light absorption in the metal) and $\chi = \text{const}$ (strong absorption of light in the metal).

Let us note in conclusion that so far we have limited our consideration to processes involving the absorption of only one photon. But evaluations show that a multiphoton electrode photoeffect is also to be observed, and that to observe it there may not be even any need for such powerful sources of radiation as lasers. In the case of multiphoton transitions close to the threshold, the "law of five over two" is still valid. For example, the surface photocurrent for an n-photon transition can be described by the equation

$$I_n = A_0 \frac{2\hbar^2}{5k^2\omega_0^{1/2}} \left(\frac{e^2}{\hbar c}\right)^{n-1} \chi_n (n\omega - \omega_0)^{5/2}, \tag{13}$$

provided $\hbar(n\omega - \omega_0) \gg kT$. The quantity χ_n is proportional to I^n (where I is the intensity of radiation), which makes it possible to distinguish experimentally transitions involving absorption of various numbers of photons.

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