U.D.C. 541.14

# Photoemission of Electrons from Metals into Electrolyte Solutions

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Photoemission of electrons from a metal into an electrolyte solution occurs when the metal is irradiated with sufficiently energetic light quanta through a layer of the solution. The emitted electrons become solvated and take part in various chemical and electrochemical reactions. Hence, photoemission studies in electrochemical systems can form the basis of a method for investigating the kinetics of various reactions, the structure of the electrical double layer at the metal-electrolyte interface, and the behaviour of electrons in liquids.
The theory of photoelectron emission, the relevant experimental techniques, and the most important results obtained in this new branch of electrochemistry are discussed. 117 references.

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## I. INTRODUCTION. HISTORICAL REVIEW OF THE PHOTOEFFECT IN ELECTROCHEMICAL SYSTEMS

The phenomena which have been termed photovoltaic (and photogalvanic) at the boundary between a metal and an electrolyte solution have been studied for over 130 years. In 1839 Becquerel found[1] that the potential of metal electrodes immersed in salt solutions or in solutions of acids or alkalies is affected by illumination. This effect, known as the "Becquerel effect", has been the object of detailed studies†. It is clear, from the multiplicity of systems which have been examined and of explanations which have been put forward, that the "Becquerel effect" is a complex combination of different phenomena. Only recent progress in photoelectrochemical research has made it possible to separate the effect into its "component elements".

The revival of interest in photoelectrochemistry in the early 1960's was due to the efforts of three workers, each of whom put forward his own explanation of the origin of the photocurrent (or of the photopotential)‡.

Berg studied the effect of light[11-20] on the dropping mercury electrode by the standard techniques of polarographic analysis ("photopolarography"). He ascribed the appearance of a photocurrent to the increase in the energy of an electron within a metal resulting from the absorption of light by the metal. The probability of electron transfer from the metal to ions or molecules is enhanced on such a "hot" electrode, and hence the rate of electrochemical reactions becomes greater.

According to Heyrovský[21-26], the photo-effect is associated with the decomposition (under the influence of light) of a surface charge-transfer complex formed by the metal electrode with molecules of the solvent (water, ethanol, etc.) or of the solute. The polarisation of the chemical bond in a complex of this type can be of either sign, depending on the electron donor or acceptor properties of the adsorbate. Absorption of a light quantum can break this bond: the bonding electrons are transferred either to the electrode (anodic photocurrent) or to the absorbed molecule, which then migrates away from the electrode surface (cathodic photocurrent). It should be noted that the idea of photodesorption or photodecomposition of a surface compound as the elementary act in photogalvanic processes is implicit in the earlier work of Veselovskii[27].

Lastly, Barker showed[28,29] that over some ranges of light frequency and electrode potential the primary process consists in electron transfer from the metal to the solution (the external photoeffect).

Strictly speaking, the concept of photoemission of electrons in the metal–electrolyte system is not new: it was first put forward in the 1920's to account for the photopotential of a number of metals[30] and for the effect of light on the rate of decomposition of alkali metal amalgams[31,32]. The same concept is found in the work of Berg[33,34]. However, only Barker was able to prove (albeit by indirect but reliable methods) the reality of photoemission into solutions and to delineate the actual limitations of the concept. Barker's work stimulated further experimental and theoretical developments in the study of photoemission into solutions, and in particular it led to the formulation of a quantum-mechanical theory of the effect (Brodskii, Gurevich, Levich[35-41]).

These three hypotheses have been considered to be mutually incompatible. However, we now have grounds to believe that each can be applied over a particular range of experimental conditions.

† The early work has been reviewed by Copeland and coworkers[2]. The work of Bowden[3], and of Hillson and Rideal[4], on the influence of light on the rate of cathodic hydrogen evolution deserves a special mention.

‡ We shall not be concerned with phenomena associated with the absorption of light by the solution, which give rise to homogeneous photochemical reactions. In this case the change in potential (or current) at the electrode is simply due to the photolysis products, excited molecules, etc. (see, for example, Refs.5 and 6). The following photoelectrochemical processes are also beyond the scope of the present review: processes on semiconductor electrodes[7,8], on metals covered with semiconducting oxide films[9], and on "insulator" electrodes[10].

This review is concerned with the present state of the theory of photoemission into solutions§. A few photoelectrochemical phenomena not involving photoemission but frequently associated with it are briefly considered in Section VI.

## II. THEORY OF THE EXTERNAL PHOTOEFFECT AT THE METAL–ELECTROLYTE INTERFACE

### 1. Photoemission of Electrons into Electrolyte Solutions

Photoemission at the metal–electrolyte interface differs in a number of important respects from the photoemission of electrons from a metal into a vacuum. Processes involving photoelectrons can be divided[29,35] into the following consecutive steps (Fig. 1): 1) intrinsic photoemission, i.e. the transfer of an electron through the interface following the absorption of a light quantum by the metal; 2) thermalisation and solvation of the electron, which lowers the energy of the emitted electron to thermal values and results in the formation (in times of the order of $10^{-11}$ s[44,45]) of a solvated electron¶; 3) chemical reaction between the solvated electron and species with electron-capturing properties present in solution (electron acceptors). The commonest acceptors are the ions $H_3O^+$ and $NO_3^-$, the molecules $O_2$ and $N_2O$, etc.

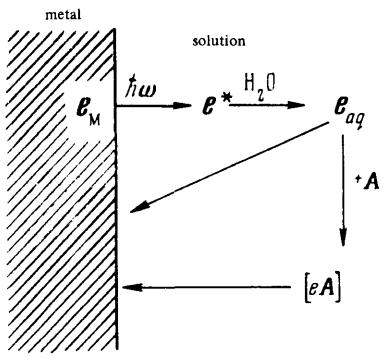



**Figure 1.** Processes occurring in photoemission.

In the absence of acceptors, the solvated electrons are quickly recaptured by the electrode, and the net photocurrent is approximately zero†. Thus, photocurrents in solutions (unlike photocurrents in the metal–vacuum system) can be observed experimentally only in the presence of electron acceptors.

Because there is an electrical double layer at the metal–electrolyte interface, where practically the whole of the externally applied potential difference appears, a new photoemission parameter has to be considered: the electrode potential. (This parameter is not relevant to the metal–vacuum interface.) The emission properties of the electrode can be drastically altered by varying the electrode potential‡.

Lastly, the work function of an electron is lower for the metal–electrolyte than for the metal–vacuum transition, because the electron gains interaction energy when it is emitted into a condensed medium. The motion of the electron in solution during the period preceding thermalisation and solvation is also different from the motion of an electron in a vacuum.

The photoemission of electrons from a metal into an electrolyte solution shows features similar to those of electrochemical reactions: both types of electron transfer reaction at the metal–electrolyte interface are described by essentially similar fundamental laws.

### 2. Quantum-mechanical Theory of Photoemission

The general theory of photoemission phenomena, including emission into electrolyte solutions, was developed by Brodskii and Gurevich[35–41]. Previous theories had a limited, phenomenological approach (Fowler's theory, for example[55,56]), and included a number of artificial assumptions or relied on models of doubtful generality[57,58]. Measurements of photoemission into a vacuum at frequencies close to the threshold value $\omega_0$ agree very well with Fowler's parabolic law[56] $I \sim (\omega - \omega_0)^2$. However, attempts to apply Fowler's theory to photoemission into an electrolyte have been unsuccessful[29,59].

The modern quantum-mechanical theory of photoemission phenomena at the metal–electrolyte interface has been discussed in detail by Brodskii and Gurevich[41], and in this review the discussion will be confined to the underlying physical concepts.

Let a semi-infinite metal sample ($x < 0$) be irradiated with light of frequency $\omega$ (Fig. 2). Energies will be measured relative to that of an electron in solution, and the thickness of the layer affected by surface forces at the interface will be denoted by $\delta$. In the present case, the thickness $\delta$ is that of the electrical double layer. The work function for the transfer of an electron from the metal to the solution is equal (but opposite in sign) to the energy of an electron at the Fermi level.

The current density of the emission from a microscopically uniform metal surface can be expressed in the form[41]

$$I = \int J(E, p_\parallel, A) \frac{1}{e^{\frac{E-\mu}{kT}} + 1} \rho(E, p_\parallel) dE dp_\parallel. \qquad (1)$$

§ A simplified treatment of the problem can be found in the semi-technical literature[42,43].

¶ The formation of a hydrated electron in aqueous solutions, first suggested by Platzman[46] in 1953, can now be taken as established. In particular, the hydrated electron appears as an intermediate in radiation-chemical and photolytic reactions. Many publications and monographs[45,47–51] have dealt with the methods of preparation of solvated electrons, their physicochemical properties, and their reactivity.

† The hydrated electron can undergo further reaction with a water molecule: $e^-_{aq} + H_2O \rightarrow H + OH^-$. However, the rate of this reaction is very slow, and in practice the electron can reach the electrode before interaction with $H_2O$ can occur.

‡ At very negative potentials (for example, on mercury in alkaline solutions) thermal emission of electrons from the metal into the solution cannot be excluded[52,53]. The resulting hydrated electrons can be treated as intermediates in cathodic electrochemical reactions. However, a more recent analysis[54] has shown that the probability of thermo-electron emission into aqueous solutions is very low.

In this expression, $E$ and $p_{\parallel} = \{p_y, p_z\}$ are the energy and the momentum (in a direction parallel to the surface) of the emitted electrons; $A$ is an arbitrary term which allows for interactions with any external electromagnetic field; $J(E, p_{\parallel}, A)$ is the asymptotic value (i.e. at a point far removed from the metal surface) of the partial current density; $\rho(E, p_{\parallel})$ is the function which describes the distribution of the density of states for the electrons in the metal; $\mu$ is the chemical potential of the electrons.

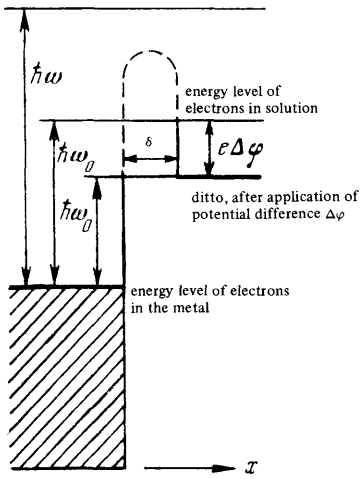



**Figure 2.** Electronic energy level diagram for photoemission from a metal into an electrolyte.

The limits of integration with respect to $E$ and $p_{\parallel}^2$ are obtained from the law of conservation of energy:

$$p = \sqrt{2m(E + \hbar\omega) - p_{\parallel}^2}, \tag{2}$$

where $p$ and $m$ denote the $x$-component of the momentum and the mass, respectively, of the emitted electron. Since the partial photocurrent $J$ differs from zero only for real values of $p$, the integration must extend over all values of $E$ and $p_{\parallel}$ which satisfy the condition

$$\begin{gathered} 2m(E + \hbar\omega) \geqslant p_{\parallel}^2 \text{ or} \\ 0 \leqslant p_{\parallel}^2 \leqslant 2m(E + \hbar\omega), -\hbar\omega < E < \infty. \end{gathered} \tag{3}$$

Essentially, the quantum-mechanical problem consists in calculating the partial photocurrent $J(E, p_{\parallel})$. The motion of the electrons with an energy higher than $kT$ can be treated as the motion of free particles with an effective mass $m$; in this case the wave function of the electron far from the metal surface has the form $\psi_f = A(p)\exp(ip_x/\hbar)$. It follows from the general expression for the quantum-mechanical current density operator [60] that our expression for $J$ must be of the form

$$J = e(p/m)|\psi_f|^2. \tag{4}$$

The function $|\psi_f|^2$ can be treated as independent of the momentum of the emitted electron as long as its kinetic energy is less than $\hbar^2/2m\delta^2$. In other words, the de Broglie wavelength of the emitted electron must be greater than the thickness of the double layer,

$$\lambda > \delta. \tag{5}$$

Another condition for constant $|\psi_f|^2$ is given by the inequality

$$\hbar(\omega - \omega_0) < E_F, \tag{6}$$

where $E_F$ is the energy of the Fermi level, measured from the bottom of the conduction band. The significance of inequality (6) is the following: the frequency of the light is so close to the threshold frequency that only those electrons within $\hbar(\omega - \omega_0)$ of the Fermi surface can take part in the photoemission process.

Eqns. (5) and (6) are the conditions for the threshold approximation, which allows the problem to be solved without reference to any specific model of the metal or of the interface. This approach has been used to discuss quantum-mechanical threshold phenomena [61].

Image forces, which operate at long range, play an important role in electron emission into a vacuum. At sufficiently low energies, $|\psi_f|^2 \sim p^{-1}$ and $J = \text{const}$ [35,37]; this justifies Fowler's approach, which involves substituting into Eqn. (1) some constant (for $p > 0$) or zero (for $p < 0$) instead of Eqn. (4).

However, when the electrons are emitted into an electrolyte, and conditions (5) and (6) apply, $J = \text{const} \cdot p/m$, and the electron density in the metal can be treated as constant to a first approximation and equal to the electron density at the Fermi surface.

Inserting the value of $J$ into Eqn. (1), and simplifying, gives the following expression for the density of the emission current:

$$I = A_0\left(\frac{kT}{\hbar\omega}\right)^{1/2} T^2 \chi \int_0^{\infty} \frac{u^{3/2}}{e^{u-\beta} + 1} du. \tag{7}$$

where $A_0$ is Sommerfeld's constant, equal to 120 A cm$^{-2}$ deg$^{-1}$, $\chi$ is a dimensionless function depending on the properties of the metal and the interface, and $\beta = \hbar(\omega - \omega_0)/kT$. At $T = 0$,

$$I = 0 \qquad \text{for } \omega < \omega_0, \tag{8a}$$

$$I = A_0\chi \frac{2\hbar^2}{5k^{5/2}\omega^{1/2}}(\omega - \omega_0)^{5/2} \qquad \text{for } \omega > \omega_0. \tag{8b}$$

Eqn. (8) shows that Fowler's parabolic law for the photocurrent as a function of frequency close to the threshold value is replaced by a "five-over-two" law. Formula (8b) applies also at ordinary temperatures if $\hbar(\omega - \omega_0)/kT \gg 1$.

The current–voltage characteristic for the photocurrent can be obtained by allowing for the effect of the electrode potential on the electron energy in the metal. A negative shift of the potential by $\varphi$ raises the Fermi level of the metal by $e\varphi$. Thus, the electronic work function from the metal into the solution varies linearly with potential: $\hbar\omega_0(\varphi) = \hbar\omega_0(\varphi{=}0) + e\varphi$. Hence, the current–voltage characteristic takes the form

$$I \simeq A(\hbar\omega - \hbar\omega_0 - e\varphi)^{5/2}. \tag{9}$$

The work function $\hbar\omega_0$ applies for $\varphi = 0$, and is (of course) a function of the chosen reference electrode.

It follows from the inequality (5) that the "five-over-two law" should hold only in concentrated solutions of electrolytes ($\geqslant$ 0.1 M). In dilute solutions the thickness of the double layer is greater than the wavelength of the electron, and condition (5) is not satisfied. If the thickness of the diffuse part of the double layer is much greater than the de Broglie wavelength, the final state of the emitted electron in solution will be altered by an amount

$-e\psi_1$, where $\psi_1$ is the potential at the outer Helmholtz plane. Therefore we must re-write Eqn. (9) in the form

$$I \simeq A\,[\hbar\omega - \hbar\omega_0 - e(\varphi - \psi_1)]^{3/2} \qquad (10)$$

(which in any case is correct for $\psi_1 > 0$). In dilute solutions, therefore, we expect a linear relationship between $I^{0.4}$ and $(\varphi - \psi_1)$. Thus, the "five-over-two law" applies also to dilute solutions, but the electrode potential in this case must be "corrected" by subtracting the $\psi_1$ potential. An analogous correction of the $\psi_1$ potential appears also in the electrochemical kinetic equations[62]. In both cases (photoemission and discharge at the electrode) the rate of the electron transfer process is controlled by $\varphi - \psi_1$ rather than by $\varphi$.

A quantitative analysis of photoemission, allowing for the finite thickness of the fixed part of the double layer[63], has yielded an expression for the photocurrent which differs from the five-over-two law only in having an additional factor depending on the potential and on the energy of the light quantum. The deviation of the photocurrent from the five-over-two law at high potentials can be used to calculate the thickness of the fixed part of the double layer.

Lastly, Brodskii and Gurevich[41,64] have developed a multiphoton theory of the external photoeffect.

### 3. Theory of Photodiffusion Currents[29,65,66]

As stated above, the photoemission of electrons from a metal into an electrolyte is accompanied by successive steps leading to the formation of solvated electrons in solution. The products of the reaction between the electrons and acceptor species in solution can take part in electrode reactions. This process gives rise to "photodiffusion" currents in solution, resulting from discharge of the solvated electrons and their reaction products. The observed photocurrent, corrected for the backward migration (towards the electrode) of the solvated electrons and their reaction products, is described (at steady state) by the equation§

$$j = \nu \int_0^\infty f(x)\{1 - \exp[-(kc/D_e)^{1/2}x]\}dx. \qquad (11)$$

The function $f(x)$ of the electron source describes the rate of formation of solvated electrons as a function of distance from the electrode; $k$ is the rate constant for the reaction between electrons and acceptors (present in solution at concentration $c$); $D_e$ is the diffusion coefficient of the solvated electron; the stoichiometric number $\nu$ characterises the reactions, at the electrode and in solution, of the products formed by the capture of solvated electrons. For example, $\nu = 0$ corresponds to oxidation of free radicals formed by electron capture, and $\nu = 2$ corresponds to reduction of these radicals with emission of one additional electron from the electrode for each particle undergoing reduction.

At low acceptor concentrations, and noting that the source function differs from zero only in a narrow region close to the electrode, the expression for the current can be simplified by a series expansion of the exponential in Eqn. (11) to give

$$j = \nu\sqrt{kc/D_e}\,\langle x\rangle\, I, \qquad (12)$$

where $\langle x\rangle$ characterises the average distance from the electrode at which solvation occurs. It follows from formula (12) that the potential dependence of the photocurrent is the same as that of the photoemission current to the precision of the factors $\nu$ and $\langle x\rangle$. The variation of $\nu$ and $\langle x\rangle$ with potential will be discussed below by considering real examples.

If the electrode is illuminated with light of variable intensity, or polarised with a fluctuating potential, a significant difference is found experimentally between the time dependence of the photocurrent and that of the emission current. In particular, $j$ and $I$ show a phase shift whose magnitude and sign are determined by the diffusion rate of electrons and free radicals in solution and by the rate constants of the chemical reactions in the solution and at the electrode surface. The phase angles for some specific cases have been calculated[29,66].

Rotenberg and coworkers[67] have calculated the photoimpedance $Z_\varphi$ of electrochemical systems, measured at an illuminated electrode polarised with a fluctuating potential of amplitude $\varphi_0$, and defined by the expression $\varphi_0 = Z_\varphi I_0$ (where $I_0$ is the amplitude of the fluctuating photocurrent). The equivalent circuits of a cell undergoing various photodiffusion processes have been discussed by Barker and coworkers[29].

## III. EXPERIMENTAL TECHNIQUES USED IN PHOTOEMISSION STUDIES

Photoemission studies in metal–electrolyte systems are usually made by illuminating the electrode with light of 250–450 nm wavelength (quantum energy 2.5–5 eV). The most popular light sources are high-pressure mercury and xenon lamps, giving a continuous spectrum or line spectra. The required part of the spectrum is isolated with a high-intensity monochromator or with interference filters. The latter can produce a spectral band 5–10 nm wide. The cell and its associated optics are made of quartz.

Experimental assemblies for photoemission studies can be arbitrarily divided into three types (direct current, alternating current, and pulsed) according to the mode of illumination used and therefore also to the design of the measuring circuit. In assemblies of the first type the light intensity is kept constant and d.c. measuring circuits are used. For the light intensities most commonly used, the measured photocurrent densities are of the order of $10^{-6}$–$10^{-7}$ A cm$^{-2}$.

Time-modulation of the light intensity offers (in principle) a solution to two problems: the scientific problem of identifying processes in the electrochemical cell which may result in slow relaxation of the photocurrent (for example, the diffusion of reactants or of intermediates), and the experimental problem of exploiting the more convenient measuring systems based on a.c. amplifiers. In the first case, frequencies above 10 kHz are required, but in the second case it is sufficient to modulate the intensity of the light at a frequency of the order of 100 Hz, either mechanically (by inserting a rotating, perforated disk in the path of the light beam), or by modulating the power supplied to the lamp. The photocurrent (or photopotential) is measured with a selective amplifier tuned to the chosen modulation frequency. The most sophisticated

§ Eqn. (11) was obtained making the following assumptions: the emitted electron reacts with an acceptor only after being solvated; the concentration of solvated electrons is so low that interaction between these species can be ignored; no electric field exists in the solution.

apparatus of this type was described by de Levie and coworkers[68-70]. It uses a dropping mercury photocathode, with a constantly renewed surface, and the photocurrent is measured at a predetermined stage in the life of the drop. The state of the surface is monitored by measuring the components of the electrode impedance as well as the photocurrent.

The technique developed for flash photolysis[71] is used in pulsed measurements. The light source is a flash lamp, fired by discharging a condenser. The normal duration of a flash is $10^{-4}$–$10^{-3}$ s, the energy of the flash can be as high as 100 J.

We have shown, in Section II. 2, that the photoemission current density is a fundamental characteristic of the photoemission process which readily lends itself to experimental determination. For accurate measurements, the potential of the electrode must be kept constant and independent of the intensity of illumination. Under steady light, or with low-frequency modulation of the light beam, this condition is easily satisfied by practically any design of potentiostatic current source. On the other hand, a potentiostat for high-frequency or pulsed measurements is much more difficult to construct, because the low impedance of the electrode (determined by the capacity of the interfacial double layer) requires a circuit with a very low source resistance. Under these conditions, measurements are usually made in the galvanostatic rather than the potentiostatic regime (i.e. with a constant current flowing through the electrochemical cell¶), and the measured quantity is the photopotential instead of the photocurrent. Provided that the differential capacitance of the electrode is known, no difficulty arises in converting one measured quantity into the other. Delahay and coworkers[59,72] used a pulsed coulostatic apparatus to study the photoemission from stationary and dropping mercury electrodes.

Comparing the merits of the three methods, we note that steady illumination offers the simplest and most accurate measurement of photocurrent, but the method is not applicable in the presence of significant dark currents, and it cannot give any information on the relaxation processes involved. The pulse method has a low precision, and it requires correct measurements of the electrode capacity, which introduces additional uncertainty. The most universally applicable method is undoubtedly the modulated beam method.

Most of the work on photoemission published so far has been done with a dropping, or stationary, mercury electrode in aqueous solution. The most widely used electron acceptors are hydrogen ions and nitrous oxide.

## IV. EXPERIMENTAL STUDIES ON THE BASIC LAWS OF PHOTOEMISSION

### 1. Dependence of Photocurrent on Electrode Potential and Quantum Energy of the Light

As shown in Section II. 2, existing theories of the photoeffect predict different variations of the photocurrent with electrode potential and with the energy of the light quanta. According to Fowler's modified theory, used to explain some of the early experimental measurements of photoemission in solutions[29,59,72], the photocurrent is a quadratic function of the quantity $(\hbar\omega - \hbar\omega_0 - e\varphi)$. The theory of Brodskii and Gurevich leads to the "five-over-two" law. Lastly, Heyrovský's model (photodissociation of surface charge-transfer complexes) predicts an exponential dependence of the photocurrent on potential or quantum energy.

The inadequacy of the quadratic law when applied to photoemission in solutions was demonstrated by Gurevich and coworkers[35]. The first experimental test of the "five-over-two" law was reported by Korshunov and coworkers[73], but these workers used a pulse method without allowing for the potential dependence of the electrode capacity.

In order to provide the data for a rational choice between the "five-over-two" law and Fowler's law, measurements of photocurrent have been made[74,75] as a function of potential under steady illumination, i.e. under conditions likely to yield the required precision and uncomplicated by considerations of double layer capacitance. The experimentally measured photocurrents were plotted in both $j^{0.5}$–$\varphi$ and $j^{0.4}$–$\varphi$ coordinates. Straight lines were drawn through the experimental points, using a computer for the least-square calculations. The intercept of the straight line on the potential axis (termed the threshold potential $\varphi_a$) was noted in each case, and used to calculate the work function of electrons in water and also the dispersion of the results (standard deviation of the experimental points from the best straight line).

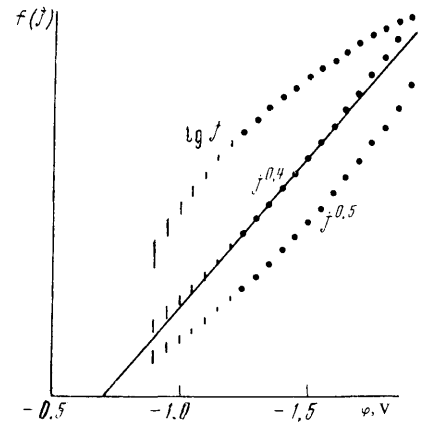



**Figure 3.** Graphical treatment of the experimental photocurrent–potential curve according to the theoretical formulae of Fowler ($j^{0.5}$), Heyrovský (lg$j$), and Brodskii and Gurevich ($j^{0.4}$). 0.1 $N$ KF solution saturated with $N_2O$; light of 436 nm wavelength[70].

The dispersion was found to be much lower for the $j^{0.4}$–$\varphi$ plot than for Fowler's $j^{0.5}$–$\varphi$ plot. On this evidence, therefore, we must conclude that the "five-over-two" law is the more satisfactory.

These results were later confirmed by other workers. Fig. 3 shows the results of photocurrent measurements[70] on a dropping mercury electrode with modulated illumination, plotted as $j^{0.4}$–$\varphi$ (according to Brodskii and Gurevich),

¶ The coulostatic method (zero current through the cell, constant charge on the electrode) is a special case of this regime.

$j^{0.5}-\varphi$ (according to Fowler), and $\lg j-\varphi$ (according to Heyrovský). It is evident from the Figure that a good straight line can be drawn only in the first plot†.

Although the reliability of the above results is lessened by occasional failure to comply with the condition of high acceptor concentration (see Section IV. 5), we may nevertheless conclude that photoemission in electrolyte solutions (in contrast to emission into a vacuum) is more accurately described by the "five-over-two" law than by Fowler's law.

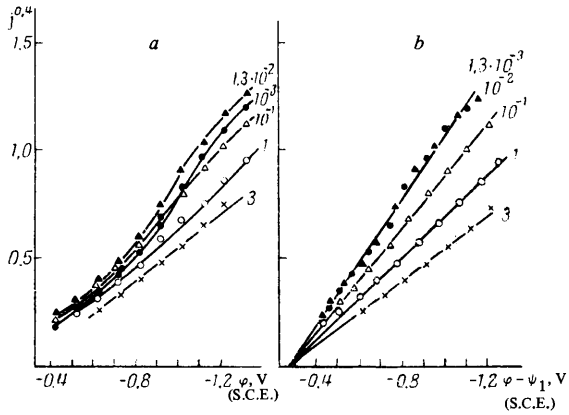



**Figure 4.** Plots of $j^{0.4}$ against (*a*) $\varphi$, and (*b*) $\varphi - \psi_1$ for KF solutions of different concentrations, saturated with $N_2O$.[76] In Figs. 4, 6, 7, 9, 10, and 13 the wavelength of light is 365 nm and the potential is referred to the saturated calomel electrode.

## 2. Photoemission into Dilute Electrolyte Solutions

The diffuse potential barrier found in dilute electrolyte solutions leads to a potential dependence of the photocurrent different from that observed in concentrated solutions (the "modified five-over-two law", Eqn. (10))‡.

Fig. 4 shows plots of the photoemission current in KF solutions at different concentrations, with $N_2O$ as the electron acceptor[76]. Straight lines in $j^{0.4}-\varphi$ coordinates are obtained only in concentrated solutions (1 M and 3 M, see Fig. 4*a*).

In Fig. 4*b* the same experimental data are re-plotted as $j^{0.4}-(\varphi - \psi_1)$. The plots now show linear portions over a wide potential region for all concentrations of indifferent electrolyte. Furthermore, all the curves can be extrapolated to the same point on the potential axis, showing that the threshold potential is the same for all concentrations. The linearity of these plots, and the fact that they can be extrapolated to the same threshold potential, are convincing evidence that Eqn. (10) can be confidently applied to dilute solutions of electrolytes§.

Similar results were reported by Korshunov and coworkers[77]. However, de Levie and Kreuser[70] found that the potential dependence of the photocurrent was satisfactorily described by Eqn. (9) in dilute as well as in concentrated solutions: the reason for this discrepancy is not clear.

An attempt has been made[78] to allow quantitatively for the drift of solvated electrons in the field of the electrical double layer in dilute solutions.

## 3. Lack of Dependence of Photoemission Threshold on the Electrode Metal and on Adsorption

When photoemission proceeds in a vacuum the "red edge" of the photoeffect depends on the electronic work function of the metal: the standard method of measuring work functions is based on this effect. By analogy, we could expect the threshold potential at the metal–electrolyte interface to be a function of the metal: in other words, the intercept at $j = 0$ of the $j^{0.4}-\varphi$ straight lines obtained for different metals should be shifted by an amount equal to the difference in work function (or in the point of zero charge) of the metals[59].

However, there is one very important difference between the metal–electrolyte and the metal–vacuum interface: the former is the seat of an additional variable—the electrode potential. Changes in electrode potential are reflected in the work function, and therefore the latter must always be referred to some defined potential. However, if we assign a potential to the electrode we simultaneously fix the initial energy level of the electron. In practice, different metals at the same electrode potential have the same Fermi level. On the other hand, the final energy level of the electron in solution is independent of the nature of the metal. The specific properties of the metal influence only the height and the shape of the potential barrier at the interface (i.e. the region of thickness $\delta$, as shown in Fig. 5). But under the conditions of the threshold approximation ($\lambda > \delta$) the properties of the barrier are irrelevant to the energetics of the photoemission process, which are determined only by the difference between the initial and the final state of the electron. Hence, the photoemission threshold in an electrolyte should be independent of the electrode metal.

This conclusion is fully consistent with the general laws of electrochemical kinetics. Indeed, the electronic work function of a metal in a vacuum does not appear explicitly in the kinetic equations if potentials are measured with respect to that of some arbitrary but constant reference electrode[79–81]. Photoemission, like any other type of electron transfer process at the metal–solution interface, must obey this law. Yet, photoemission offers a new insight into the role of the electronic structure of metals in electrochemical kinetics, because (unlike the majority of "classical" electrochemical reactions) it does not involve

† The deviations from linearity at voltages close to threshold are discussed more fully in Section IV. 5.

‡ If the measured photocurrent is lower than its limiting value, secondary effects of the $\psi_1$ potential on the photocurrent are also possible: changes in the concentration of charged acceptors near the electrode, and also drift of solvated electrons in the electric field of the diffuse part of the double layer.

§ It would be incorrect to conclude, however, that the emission of electrons proceeds only as far as the Helmholtz plane. The potential continues to vary (albeit slowly) beyond this plane. Hence, even if the point which describes the final state of the emitted electron is further from the electrode surface than the Helmholtz plane, the barrier presented by the diffuse part of the double layer remains practically impermeable to electrons, and the applicability of Eqn. (10) is unaffected.

the formation and breaking of chemical bonds, which complicate the interpretation of experimental results.

The lack of dependence of the photoemission threshold upon the nature of the metal was discovered experimentally in an investigation of mercury and of thallium and indium amalgams [74,82] (Fig. 6), and subsequently confirmed for various other metals [83]. In spite of the large difference between the points of zero charge of the metals examined (up to 0.4 V), the photoemission threshold potentials are indistinguishable within experimental error (±0.03 V).

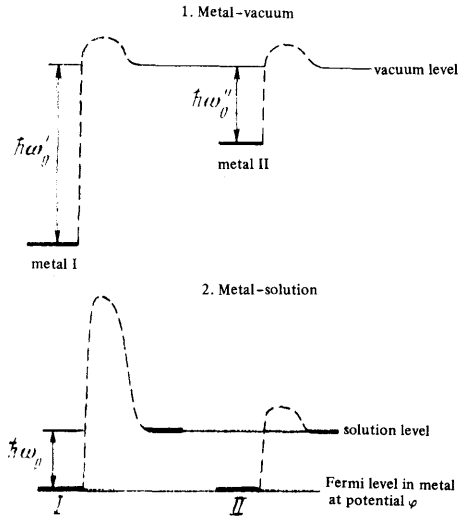



**Figure 5.** Energy diagram for photoemission into electrolytes from metals with different work functions.

Specific adsorption of surface-active ions or molecules is also not expected to shift the photoemission threshold provided that the condition $\lambda > \delta$ is not violated, i.e. as long as the thickness of the adsorption layer remains smaller than the wavelength $\lambda$ of the emitted electron. (This wavelength is ~ 10 Å for an electron energy of ~ 1 eV.) For example, with the relatively small halide ions the conditions are satisfied and the photoemission threshold of a mercury electrode is practically unaffected by adsorption (Fig. 7) in spite of significant changes in the point of zero charge¶. Similar results were obtained for the adsorption of small organic molecules [70,84]. Adsorption of organic molecules with long carbon chains invalidates the condition $\lambda > \delta$ and (as expected) influences the potential dependence of the photocurrent. Thus, photoemission experiments can provide information on the extent of adsorption and on the characteristics of the adsorbed layer [85,86].

¶ The reported [72] shift in threshold following adsorption of halide ions on mercury is due to a misunderstanding. The shift was observed in the so-called "rational" potential scales for the adsorption of halide ions, and was effectively equal to the difference between the origins of these scales. When the results are recalculated for a common reference electrode the shift in photoemission threshold for different ions almost completely disappears.

## 4. Influence of Polarisation of the Light on the Photoemission Current

A characteristic feature of photoemission, which distinguishes it from other photoelectrochemical phenomena (such as photodissociation of surface charge-transfer complexes), is its sensitivity to polarisation of the light.

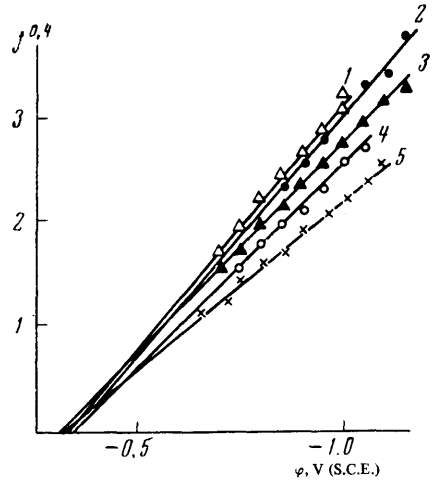



**Figure 6.** $j^{0.4}$–$\varphi$ curves for different metals: *1*) mercury, *2*) thallium amalgam (3%), *3*) indium amalgam (18%), *4*) indium amalgam (50%), *5*) lead [74].

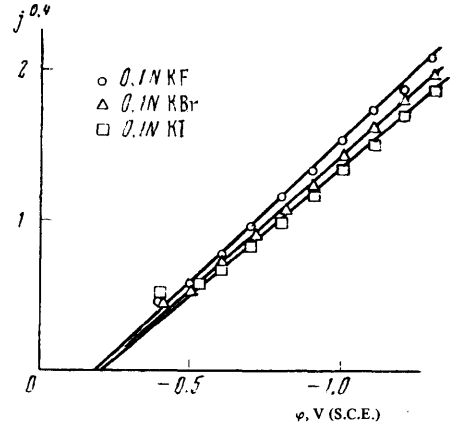



**Figure 7.** $j^{0.4}$–$\varphi$ curves for a mercury electrode in 0.1 N solutions of KF, KBr, and KI saturated with $N_2O$. [84]

An electron cannot emerge from the metal after absorption of a light quantum unless its momentum in a direction perpendicular to the interface is greater than zero. It follows from the law of conservation of momentum that the transition can be induced only by the $x$-component of the electric vector. The absorption of a wave which is polarised in the plane of the surface cannot generate a

significant amount of photocurrent. Hence, we expect the photocurrent to increase with the projection of the electric vector on the normal to the metal surface ($j \sim \sin^2\theta \cdot \cos^2\psi$, where $\theta$ is the angle of incidence of the light and $\psi$ is the polarisation angle in the plane of incidence, see Fig. 8).

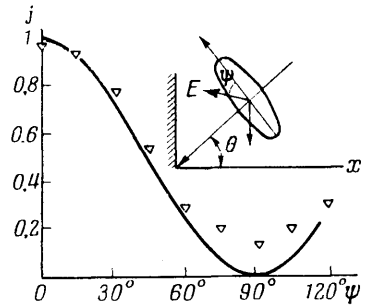



**Figure 8.** Effect of polarisation of the light on photoemission. Mercury electrode in 0.1 $N$ $K_2SO_4$ solution (open triangles). The full curve is a plot of $\cos^2\psi$.[88]

The variation of photoemission current with polarisation of the light, which had been previously observed experimentally at the metal–vacuum interface[87], has been reported also in electrochemical systems[31,32,70,88]. Fig. 8, reproduced from the paper by Korshunov and coworkers[88], shows the photocurrent at a mercury electrode in $K_2SO_4$ solution saturated with $N_2O$ (electron acceptor) as a function of the polarisation angle $\psi$ of the light (for a fixed value of $\theta$). The relatively small discrepancy between the experimental points (triangles) and the expected $\cos^2\psi$ law (solid line) is obviously due to incomplete polarisation of the incident light.

Experiments with polarised light allow us to separate photoemission from other concomitant photoelectrochemical processes which do not show polarisation selectivity (photoeffect in the bulk electrolyte, photodissociation of charge-transfer complexes, etc.).

## 5. Photoemission into Solutions with Low Concentrations of Electron Acceptors

If the concentration of acceptors is insufficient, some of the emitted electrons will be recaptured by the electrode and the measured photocurrent will be smaller than the true emission current. The expected proportionality (at low acceptor concentrations) between the photocurrent and the square root of acceptor concentration (Eqn. (12)) has been observed experimentally[29,59,78,89-91]. The proportionality coefficient can be used to assess the mean distance $\langle x \rangle$ from the electrode surface at which hydrated electrons are formed in solution. In concentrated electrolyte solutions (0.1–1 M) this distance is found[89,90] to be ~ 20 Å, but as the ionic strength of the solution decreases $\langle x \rangle$ appears to increase to ~ 100 Å.[89]

The calculated value of $\langle x \rangle$ is a mean over the whole energy spectrum of the emitted electrons for given values of $\varphi$ and $\hbar\omega$. The function $f(x)$, i.e. the distribution of velocities of the solvated electrons along the coordinate $x$, can be evaluated in principle from the dependence of the photocurrent on the concentration of acceptors (at intermediate concentrations), or alternatively from relaxation experiments[92]. The calculation has not yet been attempted, because of the inadequate precision and reproducibility of photocurrent measurements[78], but it may already be stated that $\langle x \rangle$ increases with the electron energy $E$, since $\langle x \rangle$ increases when the potential is shifted towards more negative values (for $\hbar\omega$ = const.)[29,89]. It should be noted that Korshunov and coworkers[90] arrived at the opposite conclusion from their measurements of photocurrent as a function of electrode potential and acceptor concentration. But we must stress that the precision of measurements on concentration dependence is often suspect. A more reliable argument for the dependence of $\langle x \rangle$ on electron energy is the experimentally observed shift[93] of the threshold potential (found by extrapolating the $j^{0.4}$–$\varphi$ straight lines) on increasing the concentration of acceptors in solution (Fig. 9).

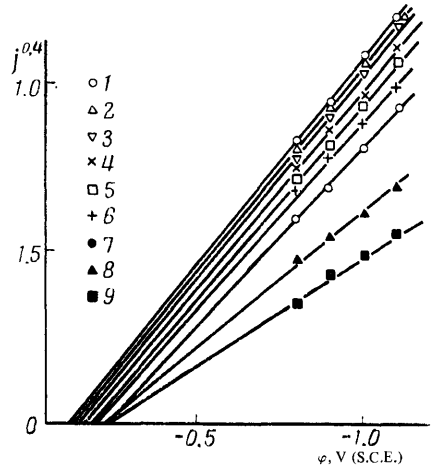



**Figure 9.** Effect of acceptor concentration ($H_3O^+$) on the apparent photoemission threshold: *1*) 0.42, *2*) 0.25, *3*) 0.11, *4*) 0.063, *5*) 0.044, *6*) 0.03, *7*) 0.018, *8*) 0, *9*) 0.0012 mole litre$^{-1}$.[89]

This shift does not imply a change in the "true" work function of the electrode metal with respect to the electrolyte; it is merely the result of a change in the dependence of the photocurrent on potential as the concentration of acceptors is varied but the method of graphical interpretation of the results is kept unchanged. By assuming an explicit form of the function $\langle x \rangle$ ($E$) we can calculate a $j$–$\varphi$ curve which is not described by the "five-over-two" law. The positive deviations from this law (see Fig. 3) have been explained qualitatively by these arguments.

As already stated, the precision of present-day experiments is insufficient to calculate the functions $f(x)$ and $\langle x \rangle$ ($E$). The greatest accuracy is obtained in measurements of photoemission at high acceptor concentrations, when diffusion processes play only a minor role[78,93].

The true photoemission threshold has been determined[93] by correcting the apparent shift due to diffusion of hydrated electrons, and used to calculate the work function for electron emission from mercury into water at the zero-charge potential (3 eV). (This value is lower by 0.2–0.3 eV than the previously accepted value[73,74], which did not

include a diffusion correction.) The lower work function of mercury in water as compared with the vacuum value (4.5 eV) is due, as we have already pointed out, to the interaction of a super-thermal electron with the polar solvent medium. The lowering (1.5 eV) is less than the hydration energy of the electron (1.7 eV[45]). Hence, the final state of the photoemission process is a quasi-free electron rather than a fully thermalised and hydrated electron.

The electronic work function in other solvents, measured by the photoemission method, has also been found to be lower than the work function in a vacuum. The lowering is close to the energy of the electronic polaron in these solvents, and is evidently due to the electronic polarisation of the medium by the emitted electron[82].

### 6. The Multi-photon Effect

The experiments discussed above relate to the one-photon photoeffect, in which the energy of a single light quantum is sufficient to cause photoemission. Korshunov and coworkers[94] discovered two- and three-photon external photoeffects at the mercury–solution interface. A laser was used as the light source: a ruby laser in the first case (quantum energy $\hbar\omega = 1.78$ eV), and a neodymium laser in the second ($\hbar\omega = 1.18$ eV). As in the one-photon effect, the photocurrent varies with potential according to the "five-over-two" law. The relationship between the photocurrent and the light intensity is, as expected from the theory, an exponential function with an exponent approximately equal to the number of photons absorbed for every emitted electron.

## V. PHOTOEMISSION AS A METHOD OF STUDYING THE KINETICS OF CHEMICAL AND ELECTROCHEMICAL REACTIONS

When electrons are emitted into a solution as a result of irradiation, many processes in which the solvated electrons are involved in further transformations can occur in the layer of solution adjacent to the electrode. The most interesting of these are homogeneous and heterogeneous reactions involving free radicals. The kinetics of these reactions are reflected in the magnitude of the experimentally measured photocurrent, and therefore we may think of photoemission as a convenient method of monitoring such processes. We shall limit the discussion to the simplest systems, for which quantitative experimental data are available.

### 1. Kinetics of the Electrochemical Conversion of Atomic Hydrogen at a Mercury Electrode

Atomic hydrogen is formed in solution by the capture of a hydrated electron by a hydrogen ion:

$$e^-_{aq} + H_3O^+ = H + H_2O. \qquad (A)$$

The hydrogen atom undergoes reduction over a wide range of potentials (from −0.7 to −1.5 V against the saturated calomel electrode)

$$H + HS + e^- = H_2 + S. \qquad (B)$$

In the above equation the symbol HS denotes a source of protons, which could be $H_3O^+$ or $H_2O$. At more positive potentials the ionisation of atomic hydrogen becomes increasingly important

$$H + H_2O = H_3O^+ + e^-, \qquad (C)$$

leading to a drop in the measured cathodic photocurrent (first observed by Barker[29]).

We shall outline the results of some kinetic studies of the conversion of atomic hydrogen, obtained from photoelectrochemical measurements[95,96]. Photoemission is used as a source of atomic hydrogen in the region of the electrode surface: the procedure is more convenient than others used so far[97–99].

The photocurrent experimentally measured in the electrochemical system is defined by the expression $j = j_0 + \vec{j} - \overleftarrow{j}$, where $j_0$ is the emission current (not including the current of electrons recaptured by the electrode without having reacted), $\vec{j}$ is the cathodic current of reaction (B), $\overleftarrow{j}$ is the ionisation current of atomic hydrogen. The variation of $j_0$ with potential, as already stated, has approximately the form $j_0 \sim (\varphi - \varphi_a)^{5/2}$, where $\varphi_a$ is the threshold potential for light quanta of a given energy.

A hydrogen atom can take part in reactions (B) and (C) either in an adsorbed state at the surface of the metal or in the layer of solution adjacent to the electrode.

At negative potentials, when the rate of oxidation of the H atom can be ignored, $j = 2j_0$, and the experimental dependence of the photocurrent on potential is (to a first approximation) the same as that of the emission current. In the more general case, when reaction (C) cannot be neglected, the photocurrent $j$ is given by the expression[96]

$$\varphi = \frac{2.3RT}{(\alpha+\beta)F}\left[lg\left(\frac{2j_0}{j} - 1\right) + lg\frac{\varkappa_1}{\varkappa_2}\right], \qquad (13)$$

where $\alpha$ and $\beta$ are the transfer coefficients of reactions (B) and (C) respectively, and $\varkappa_1$ and $\varkappa_2$ are the rate constants of these reactions at $\varphi = 0$†.

Eqn. (13) predicts a linear relationship between $\varphi$ and $\lg(2j_0/j - 1)$, with a slope determined by the transfer coefficient of the appropriate reaction. The current $2j_0$ (in the absence of oxidation of the atomic hydrogen) can be found either by extrapolating the linear portion of the $j^{0.4}$–$\varphi$ plot to the potentials where non-linearity sets in owing to the oxidation of hydrogen (see Fig. 10), or by measuring the photocurrent with a different acceptor, reacting with the hydrated electron to give products which are not oxidised at the electrode. One such acceptor is nitrous oxide, which forms the $OH^\cdot$ radical after capturing an electron. This radical is reduced at the electrode to the hydroxyl ion over the whole of the accessible range of potential.

Fig. 10 shows some plots of the photocurrent ($j^{0.4}$) against potential in KCl, KBr, and KI solutions containing 0.01 g-equiv. litre$^{-1}$ of HCl. The relationship is linear at negative potentials, and the deviations from linearity (i.e. decrease in photocurrent) set in at increasingly negative potentials on going from $Cl^-$ to $I^-$. It is evident from Fig. 10 that specific adsorption of the iodide ion has a strong positive effect on the anodic current $\overleftarrow{j}$ (as compared with the cathodic current $\vec{j}$). The experimental data for all solutions give linear plots in $\varphi$–$\lg(2j_0/j - 1)$ coordinates, thus confirming the correctness of Eqn. (13). The slopes of these straight lines (100–120 mV) indicate that $\alpha + \beta = 1/2$, i.e. the transfer coefficient of one of the

† The logarithmic term $2j_0/j - 1$ is identically equal to $j/\vec{j}$.

conjugated reactions is zero and hence its rate is independent of potential. Additional information on the mechanism by which atomic hydrogen is removed from solution can be obtained from the effect of pH in decreasing of photocurrent.

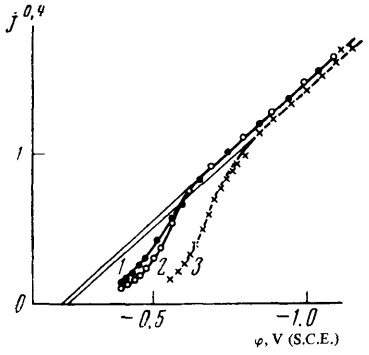



**Figure 10.** Effect of oxidation of H on the photocurrent. Mercury electrode in 0.1 *N* solution of: *1*) KCl, *2*) KBr, and *3*) KI containing 0.01 *N* HCl.[96]

Fig. 11 shows the variation of the potential $\varphi^*$, at which $\vec{j} = -\vec{j}$‡, with the concentration of hydrogen ions, over the $c_{H_3O^+}$ range between $10^{-3}$ and 1 *N* in solutions containing a total concentration of electrolyte of 1 *N*. As the Figure shows, $\varphi^*$ increases monotonically with acidity, the increase being most marked in the most strongly acid solutions. At low acid concentrations ($10^{-2}$–$10^{-3}$ *N*) $\varphi^*$ is practically independent of pH.

From these results it was concluded[96] that two mechanisms of hydrogen removal are possible: the two conjugated reactions proceed without an adsorption step, or both reactions involve adsorbed hydrogen, in which case one of the reactions is non-activated§. Further experimental data are needed to identify the potential-independent reaction: in particular, we need information from other metals, having a hydrogen adsorption energy different from that of mercury.

The variation of the $\varphi^*$ potential with pH suggests a new type of electrochemical desorption, involving hydrogen ions and water molecules simultaneously¶. The removal of adsorbed hydrogen by an electrochemical mechanism involving water molecules in acid solutions was first considered by Krishtalik[102].

Specific adsorption of anions accelerates the ionisation of hydrogen (if activated) by producing a more positive potential difference across the fixed part of the double layer. At the same time, anion adsorption should accelerate the electrochemical desorption involving hydrogen ions. As Fig. 10 shows, adsorption of iodide influences ionisation more markedly than electrochemical desorption (particularly, since water takes part in the latter)†.

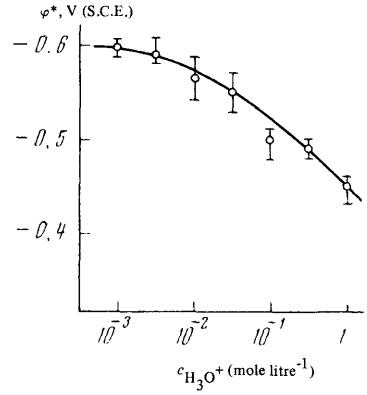



**Figure 11.** Variation of $\varphi^*$ potential with concentration of $H_3O^+$.[96]

The concept of a non-activated electrochemical reaction was first put forward in 1936[103,104], but it has not been possible so far to observe limiting currents due to non-activated discharge in direct experiments. Krishtalik's barrierless processes[100] may be quoted as an indirect experimental proof of the reality of non-activated reactions.

## 2. Homogeneous Chemical Reactions Involving Free Radicals

The most detailed studies of homogeneous chemical reactions involving the radicals H, OH[105], and $NO_3^{2-}$ [106-108] have been made by the photoemission method.

Barker[105] studied the reaction between methanol and ethanol, on the one hand, and H and OH radicals formed by the photoemission of electrons into acid solutions and into solutions containing $N_2O$, on the other hand. We know, from radiation-chemical experiments, that the H and OH radicals attack the $\alpha$-hydrogen in alcohols. The resulting RĊHOH radicals are easily oxidised at the electrode to the corresponding aldehydes. For the case of the oxidation of RĊHOH radicals, the coefficient $\nu$ which appears in the kinetic equations (11) and (12) takes the form

$$\nu = \left(1 + \frac{\sqrt{k_R \cdot c_R / D_R}}{\sqrt{k \cdot c / D_e}}\right)^{-1}, \qquad (14)$$

‡ It follows from Eqn. 13 that

$$\varphi^* = \frac{2.3\,RT}{(\alpha + \beta)\,F} \lg \frac{\varkappa_1}{\varkappa_2}. \qquad (D')$$

§ The hydrogen removal mechanism through the adsorbed state seems the more probable, since both reactions (ionisation and reduction in solution) should be non-activated at these potentials[100], and hence the experimentally observed loss of photocurrent cannot be ascribed to them.

¶ The observed variation of $\varphi^*$ with pH can be formally explained by assuming the formation (in acid solutions) of the $H_2^+$ radical, which is subsequently reduced at the electrode. However, the rate constant for the reaction between H and $H_3O^+$ is very small ($10^4$ litre mole$^{-1}$ s$^{-1}$)[101], and therefore the contribution of this reaction to the photocurrent cannot be substantial.

† The effect of iodide adsorption can be explained in a similar way by assuming that the ionisation of hydrogen is non-activated.

where $c_R$ is the concentration of alcohol present in solution, $k_R$ is the rate constant for the capture of a radical by the alcohol, and $D_R$ is the diffusion coefficient of the H or OH radical.

Eqn. (14) predicts a decrease in photocurrent in the presence of alcohol. The decrease is observed experimentally at $\varphi > -1.4$ V. At more negative potentials the photocurrent is the same as in the absence of alcohol ($\nu \to 2$). The linear relationship predicted by Eqn. (14) between the reciprocal of the current and the square root of the alcohol concentration has been satisfactorily demonstrated (Fig. 12) for the case of OH radicals. The rate constants for the reaction of OH with methanol and ethanol, calculated from the experimental results by means of Eqn. (14), are both equal to $2 \times 10^9$ litre mole$^{-1}$ s$^{-1}$. For the reaction involving H the result is $k_R = 8 \times 10^6$ litre mole$^{-1}$ s$^{-1}$.

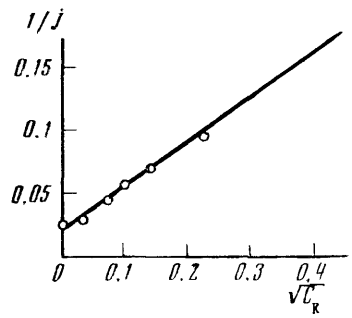



**Figure 12.** Reciprocal of the photocurrent in 0.2 $N$ KCl solution containing $N_2O$ against square root of ethanol concentration[105].

In the presence of alcohol, the variation of the photocurrent with the concentration $c$ of electron acceptors ($N_2O$ and $H_3O^+$) is also altered. When the products of the capture of H and OH by the alcohol are not oxidised at the electrode, and at low concentration of acceptors, we have $j \sim \sqrt{c}$ [Eqn. (12)]. If the RĊHOH radicals are oxidised, and the second term in Eqn. (14) is large compared with unity, we have $j \sim c$. This dependence has been observed experimentally.

Barker, using pulsed illumination, was able to monitor the kinetics of the electrochemical oxidation of RĊHOH radicals on mercury by studying the anodic photocurrent which persists after the period of illumination‡. The observed exponential decay of the anodic photocurrent was taken as evidence that the oxidation of RĊHOH radicals is preceded by an adsorption step. The rate constant of the oxidation was $\sim 10^{-3}$ cm s$^{-1}$ at −1.4 V (S.C.E.).

The rate constants for the reaction of H and OH with alcohols found by the photoemission method are in good agreement with experimental results obtained by pulse radiolysis of the same solutions[105].

‡ Levin and Delahay[109] observed anodic currents during the pulse irradiation of acid solutions in the absence of added materials. Their results have not yet been explained satisfactorily.

The chemical reactions of the ion-radical $NO_3^{2-}$ have been studied by two photoelectrochemical methods, using pulsed[106,108] and steady[95,107] illumination. This radical is formed when electrons are photo-emitted into solutions containing $NO_3^-$. The following chemical reactions take place at the electrode and in its immediate vicinity

$$\left.\begin{aligned} NO_3^- + e_{aq}^- &= NO_3^{2-} \\ NO_3^{2-} &= NO_2^- + O^- \end{aligned}\right\} \text{in solution}, \quad \begin{matrix}(D)\\(E)\end{matrix}$$

$$NO_3^{2-} = NO_3^- + e^- \quad \text{at the electrode}, \quad (F)$$

$$O^- + H_2O = OH + OH^- \text{ in solution}, \quad (G)$$

$$OH + e^- = OH^- \text{ at the electrode}. \quad (H)$$

The $NO_3^{2-}$ ion-radical is oxidised at the electrode at potentials more positive than −1.2 V leading to a decrease in the measured photocurrent[29].

A quantitative study of this reaction by Eletskii and coworkers[107] showed that two "limiting" portions appear on the photocurrent curve (at negative and positive potentials respectively). Both portions obey the "five-over-two" law, and extrapolate to the same threshold potential. Fig. 13 shows the $j^{0.4}$–$\varphi$ plot for a concentrated solution of $NaNO_3$.

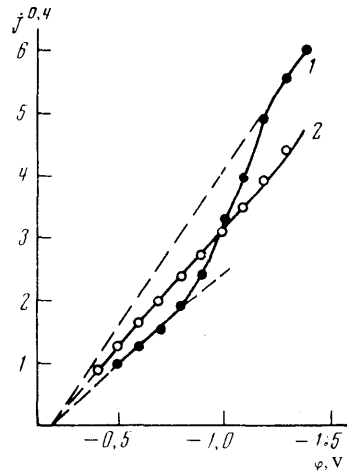



**Figure 13.** $j^{0.4}$–$\varphi$ curves in: *1*) 1 $N$ solution of $NaNO_3$ and *2*) the same solution containing $10^{-4}$ $N$ tetrabutylammonium salt[95].

The experimental results are in good agreement with the theory. Two linear portions (for high and low potentials respectively) are separated by a curvilinear portion extending from −0.7 to −1.2 V relative to the saturated calomel electrode. Small additions of tetrabutylammonium salt ($10^{-4}$ mole litre$^{-1}$) produce a marked change in the shape of the curve: all the points now lie on the same straight line at potentials more positive than −1.4 V.

The influence of tetrabutylammonium is the result of two separate effects: adsorption at the mercury surface suppresses the emission current[84], but it also inhibits the oxidation of $NO_3^{2-}$, thus suppressing the decrease in photocurrent at positive potentials. The rate constant $k_d$ for the decomposition of $NO_3^{2-}$ in solution, and the transfer coefficient $\beta$ of the electrochemical oxidation of $NO_3^{2-}$, have

been determined from the experimental results: $\beta \simeq 0.25$, $k_d = 6 \times 10^6\ s^{-1}$. A similar value of the transfer coefficient has been obtained by other workers[106,108].

A much lower value of the rate constant ($k_d = 10^4\ s^{-1}$) has been reported[106,108] from measurements of the emitted charge under pulsed illumination of the electrode. Those workers[106,108] ascribe the increase in charge in the presence of $NO_3^-$ to electrochemical reduction of the OH radicals formed from the decomposition of $NO_2^-$ by reactions (E) and (G); $k_d$ was calculated from the kinetics of this growth of charge.

It is evident, from the examples considered in this Section, that the study of photoemission phenomena in aqueous solutions offers a wealth of information on homogeneous and heterogeneous processes in the layer of solution adjacent to the electrode.

### 3. Competing Solvated-electron Capture Reactions

Competing reactions take place in solution when several electron acceptors are present together. The competing acceptor method is widely used in radiation chemistry to determine relative rate constants. Barker and coworkers[29] have made a quantitative study of the photocurrent in the presence of two competing electron acceptors (A and B).

| Acceptors | | $10^{-10}k_A$, litre mole$^{-1}$ s$^{-1}$ | |
|---|---|---|---|
| A | B | photo-emission | pulse radiolysis |
| $H_3O^+$ | $N_2O$ | 1.5 | 1.4 |
| $Zn^{2+}$ | $H_3O^+$ | 0.046 | 0.06 |
| $Cd^{2+}$ | $N_2O$ | 3.6 | 2.1 |
| $Ni^{2+}$ | $N_2O$ | 1.5 | 0.9 |
| $NO_3^-$ | $N_2O$ | 2.0 | 1.76 |
| $NO_2$ | $N_2O$ | 0.5 | 0.63 |

In the general case, the dependence of the photocurrent on the concentration of the two acceptors ($c_A$ and $c_B$) can be written in the form

$$j = j_0(\nu_A k_A c_A + \nu_B k_B c_B)/(k_A c_A + k_B c_B)^r. \qquad (15)$$

In this expression $k_A$ and $k_B$ are the rate constants for the reaction of electrons with the acceptors A and B respectively, $\nu_A$ and $\nu_B$ are the stoichiometries for these reactions. The exponent $r$ depends on the concentration of acceptors. At high acceptor concentrations $r = 1$; when both $c_A$ and $c_B$ are low $r = 1/2$. Eqn. (15) is strictly applicable if the stoichiometries $\nu_A$ and $\nu_B$ are independent of acceptor concentration. Furthermore, the product of the reaction of an electron with one of the acceptors must not undergo further reaction with the other acceptor.

It follows from Eqn. (15) that the ratio of the rate constants ($k_A/k_B$) can be determined by studying the variation of the photocurrent with the concentration of both acceptors. The absolute values of the rate constants can be deduced from the relative value if the rate constant of one of the competing reactions is known. Absolute values of the rate constant for the capture of a hydrated electron by various acceptors, measured by the photoemission variant of the method of competing reactions, are listed in the Table[29]. The values obtained by the pulse radiolysis method are also given for comparison.

In the calculations the absolute rate constant $k_{N_2O}$ was taken, on the basis of radiation-chemical measurements, as $5.6 \times 10^9$ litre mole$^{-1}$ s$^{-1}$. The satisfactory agreement between the two methods is evident from the Table.

## VI. SOME NON-EMISSION PHENOMENA ASSOCIATED WITH THE EXTERNAL PHOTOEFFECT

As was stated above, photoemission is only one of the many photochemical effects which make up the "Becquerel effect". A brief description of some of these phenomena is appropriate here, because, like photoemission itself, they can be used to study the structure of the interface between an electrode and an electrolyte, and the kinetics of reactions at such an interface.

### 1. Anodic Photocurrents

To explain the photoeffect, Heyrovský suggested the formation of a charge-transfer complex between the surface of a metal electrode and molecules of solvent or solute decomposed under the influence of light. This explanation cannot be applied to a mercury electrode at potentials more negative than its point of zero charge, i.e. in the region of cathodic photocurrents. In this case, photoemission is a more probable process. But at more positive potentials, where emission is inconceivable and the observed photocurrents are usually of the opposite sign (i.e. anodic), Heyrovský's explanation is probably correct. Anodic photocurrents are observed in solutions of oxalic, chloroacetic, tartaric, and other organic acids and their salts[26]. The molecules of all these compounds contain the $-\overset{\overset{O}{\|}}{C}-\overset{\overset{X}{|}}{C}-$ group, where X denotes an electronegative substituent. When these species are adsorbed at the mercury surface a chemical bond is formed between the metal (acceptor) and the O or X atom (electron donors). The resulting bond can absorb light of greater wavelength than the compound originally in solution. On illumination the adsorption bond is broken, the electrons are transferred to the electrode, and the organic substance (in an oxidised form) is returned to the solution.

A similar mechanism was invoked[110] to explain the photoeffect at a platinum electrode under the influence of u.v. light.

The study of anodic photocurrents can yield valuable information on the energy spectrum of the surface electronic levels of the metal corresponding to the adsorbed particles.

### 2. Pulse Heating of the Electrode

According to Berg, light adsorption "excites" the electrode and (in the presence of a depolariser) enhances electrochemical reactions which are hindered in the dark. The concept of a "hot" electrode has been tested by looking for evidence of light-induced changes in properties such as surface tension and differential capacitance[70,111]. No significant change in the surface properties of mercury was observed on illuminating a mercury electrode with steady light from a super-high pressure lamp. However, a change in the differential capacity (due to the heating of the electrode and the adjacent layer of solution) has been observed by using very high energy light pulses.

In dilute solutions the differential capacity of the electrode is determined mainly by the capacity of the diffuse part of the double layer, and therefore decreases with increasing temperature. In the galvanostatic and the coulostatic regime a change in capacity produces a shift in the electrode potential; in the potentiostatic regime it produces a change in the current flowing in the external circuit. In both cases the sign of the effect depends on the sign of the charge on the electrode. Korshunov and coworkers[73] have proposed a method of measuring the zero-charge potential of metals based on this effect: as the (dark) potential of the electrode is varied, the sign of the photoeffect is found to change at a value of the potential corresponding to zero charge on the electrode. Long-wave light, which does not cause photoemission, is used in this experiment§.

Other interesting photoelectrochemical phenomena, on which we shall not dwell, include electrode reactions of light-excited depolariser molecules[5,112], photoemission of electrons from the surface of electrolyte solutions into the surroundings[113], and electro-reflection at the metal–electrolyte boundary[114-116].

## VII. FUTURE PROSPECTS

The special properties of the metal–electrolyte interface (in particular, the independently variable potential of the electrode) offer a number of valuable facilities in studies of photoemission. Studies of this phenomenon in electrochemical systems can provide information on the electron density in the metal and its distribution, on the properties of the Fermi surface of the metal[117], and on the mechanism of light absorption by the metal surface.

Furthermore, photoemission studies have led to the solution of a number of purely chemical problems. For example, the structure of the electrical double layer and various adsorption phenomena have been studied in detail. The potential variation within the fixed part of the double layer can be investigated by monitoring deviations from the "five-over-two" law. Also, definite conclusions regarding the structure of the fixed part of the double layer can be based on data obtained from the study of photoemission into solutions.

Lastly, it is possible to study the behaviour of electrons in liquids, and in particular to measure the rate of solvation of electrons and the rate of capture of solvated electrons by acceptors and by the electrode surface.

Thus, the photoeffect at the metal–solution interface offers not only an insight into purely photoemission phenomena but also a powerful new method of studying the structure and properties of this interfacial boundary and the physicochemical processes of which it is the seat.

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