Photogalvanic Processes on a Gold Electrode

By *V. Veselovsky*

In a previous paper[1] we formulated the basic principles underlying the photogalvanic method of investigating electrode processes using the silver electrode as an object of investigation.

Especial interest attaches to the investigation of anode processes by this method in view of the high light sensitivity of the oxygen, halogen and other films, the formation of which often accompanies anode processes on metals and to a considerable degree determines their course.

It is expedient above all to use the photogalvanic method in studying the basic anodic processes: oxygen overvoltage and anodic passivity of metals. On the other hand, fruitful results may be expected from an application of modern electrochemical methods to the study of photogalvanic phenomena, in particular, of the ideas developed by the school of Frumkin, which establish a connection between the conditions of the electrode surface and the course of the electrode processes. It is sufficient to recall the role played in revealing the nature of the photoelectric effect by a consideration of the state of the emitting surface, in particular of the presence of adsorbed atoms on this surface.

There are only a few papers in the literature devoted to the influence of light on an anodically polarized metal. From the viewpoint of the present investigation, interest attaches to the work of Grube and Baumeister[2]. Using undispersed light these authors showed that the potential of a smooth platinum electrode submitted preliminarily to a strong anodic polarization is greatly lowered upon irradiation.

The method used by Grube (lengthy expositions, not monochromatic light) in which secondary processes took place excludes a quan-

[1] V. Veselovsky, Acta Phys. Chim., **14**, 483 (1941).

[2] G. Grube u. L. Baumeister, Z. Elektrochem., **30**, 322 (1924).

titative treatment of the results obtained. We nevertheless believe that the lowering of the potential of anodically polarized smooth platinum under the action of light may be given a sufficiently satisfactory explanation, similar to that of the photogalvanic process on a silver electrode[1]. Indeed, anodically polarized platinum is covered, like silver, with a layer of oxides, as shown by Obrucheva[3] and Armstrong, Himsworth and Butler[4]. Hence in this case, too, the photogalvanic process may consist in the photogalvanic dissociation of the surface oxygen compounds, in which negative charges are imparted to the metal with a corresponding lowering of the potential of the irradiated electrode. The reversal of sign of the effect on platinized platinum does not fit into the above scheme of the process and may possibly be due to the strong influence of secondary phenomena, in particular, to atomic oxygen formed as a result of the process.

In a paper by Bowden[5] brief mention is made of an observed lowering of the oxygen overvoltage on a platinum electrode under the action of light.

We chose gold as an object of investigation, since as compared with other metals, platinum and silver in particular, it possesses several advantages for a quantitative study of the laws of the photogalvanic process by our method.

Gold has a high oxygen overvoltage, hence it is possible to work with gold electrodes over a large range of potentials under conditions where there is no steady state volume evolution of oxygen to complicate the measurements. The large anodic passivity of gold makes it possible to carry out photogalvanic measurements on a gold electrode even at sufficiently strong anodic polarization not only in alkaline but also in acid solutions (sulphuric acid) where the formation of bulk oxides, which are soluble in acids, is excluded. Preliminary experiments with an anodically polarized gold electrode showed that gold also has a great photogalvanic activity in the visible part of the spectrum as compared with platinum.

Finally a number of investigations of the gold electrode have been made which establish the state of its surface in a sufficiently

[3] Obrucheva, Oxygen on Platinum (unpublished data).

[4] Armstrong, Himsworth and Butler, Proc. Roy. Soc., **143**, 89 (1934).

[5] Bowden, Trans. Farad. Soc., **27**, 505 (1931).

wide range of potentials. The work of Armstrong, Butler and Himsworth[4] and of Deborin and Ershler[6] proves that oxygen films are formed on gold upon its anode polarization.

In an old paper on the influence of light on anodically polarized gold, Bose and Kochan[7] established that the potential of a gold electrode, preliminarily strongly polarized anodically, is sharply lowered by the action of light. They made the qualitative observation that this effect is caused mainly by the short wavelength part of the spectrum (starting from the green region). However, the method used (polarization of the electrode for several days, expositions of several hours, filters letting through a wide band of radiation) make it extremely difficult to attempt a quantitative analysis of the results obtained. We shall touch on them briefly in discussing the results to be set forth below.

In the present investigation we set ourselves the following aims:

1. To establish the relation between the photogalvanic effect and the electrochemical characteristics of an electrode—potential, extent of surface covered by adsorbed atoms.

2. To determine the spectral sensitivity of the photogalvanic effect on an old electrode.

3. To check the applicability to photogalvanic processes of Einstein's relation of equivalence between the action of an electric field and the energy of the radiation used.

Experimental method

The experimental method of investigating the photogalvanic process on a gold electrode consists in the following.

1. Measurement of the magnitude of the photogalvanic effect of the electrode at increasing potentials (caused by polarization by a current of constant intensity).

2. Measurement of the photogalvanic effect of an electrode kept at a steady potential and subjected to brief (for a fraction of a second) irradiation by various wavelengths. From these measurements it was possible to establish the relation between the magnitude of the photogalvanic effect and the wavelength of the radiation applied.

[6] G. Deborin and B. Ershler, Acta Phys. Chim., **13**, 347 (1940).
[7] Bose u. Kochan, Z. physik. Chem., **38**, 29 (1901).

As a powerful source radiating a continuous spectrum we used an arc between two graphite electrodes. To improve the quality and constancy of the radiation only the crater of one of the electrodes placed horizontally, was projected onto the slit of the monochromator. By keeping the current in the circuit constant it was possible to get a sufficiently constant intensity of radiation for the duration of the experiment.

For prolonged experiments a 1000 w incandescent lamp was substituted for the arc. In individual experiments and for calibrating the monochromators mercury lamps (Heraeus and pointolite lamps) were used.

A narrow beam of monochromatic radiation was obtained by using a glass monochromator in the visible region and a quartz monochromator in the ultraviolet.

The monochromators were calibrated in the usual manner, mainly by known mercury lines, and in the long wavelength region by known sodium and lithium lines, obtained by introducing the corresponding salts into the flame of a Bunsen burner.

To reduce extraneous radiation, the beam of light from the source was passed before entering the monochromator, through filters which let through the desired range (including the necessary line or narrow spectral band). Infrared radiation was adsorbed by a column of water 10 cm long.

The principal instrument in the electrical measuring part of the set-up was a Cambridge string electromagnetic galvanometer with a current sensitivity of 1×10^{-10} A, a voltage sensitivity of the order of 1×10^{-6} V and a period up to 0.002 sec. With this instrument it was possible to measure the rate of increase of the electrode potential in the first hundredth fraction of a second, the measuring current not exceeding 1 % of the true photogalvanic current.

In addition to visual observation of the maximum deviation of the galvanometer thread, which could be done sufficiently accurately up to expositions of 0.1 sec., these deviations could be recorded on an Edelman oscillograph. The oscillogram then furnished an idea of the complete trend of the electrode potential under the action of light.

Short expositions were made with a «Kompur» camera shutter, corrections for the time of exposition being subsequently made from the time scale of the oscillogram (usually the known frequency of the a. c. source feeding the lamp in the oscillograph).

The reaction vessel made of transparent quartz is schematically represented in Fig. 1.

The electrode to be tested and the auxiliary electrode were sealed into ground glass joints. The tube *A* contained an auxiliary electrode for polarization made of the same material as the test

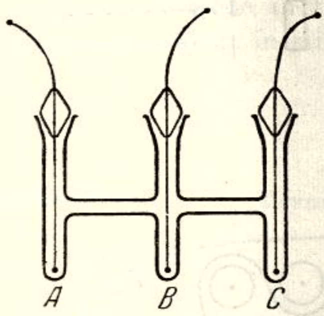

Fig. 1. Quartz reaction vessel.

electrode. The tube *C* contained an auxiliary platinized platinum electrode preliminarily strongly polarized cathodically which served to measure the potential of the test electrode.

The test electrode—a gold wire (Hilger) 1 mm in diameter—was placed in the central tube *B*. The length of this electrode was chosen in accordance with the height of the radiation beam in the slit of the monochromator. The tubes *A*, *B* and *C* communicated with one another through capillaries. To increase the efficiency of the incident radiation, tube *B* was silvered on the outside. Light fell on the test electrode through a slit left in the silverplating of the tube, coinciding with the slit of the monochromator.

The entire reaction vessel was placed in a dark chamber in such a manner that the slit of the monochromator came out directly up against the opening in the tube with the test electrode.

The polarization and potentiometry were carried out by the usual technique using calibrated precision instruments. The most essential details will be mentioned in the description of the experiments. The set-up is shown schematically in Fig. 2.

A—source of radiation, *B*—light filter, *C*—camera shutter, *D*—monochromator, *E*—reaction vessel with test electrode, *F*—string galvanometer with illuminator, *G*—oscillograph set-up.

The measuring process consisted in the following: The potential of the test electrode *B* was brought to the required value by passing a direct current through the test electrode B and the reference electrode A (Fig. 1). The potential difference between the test and reference electrodes (B and C) was measured by the compensation method, the string galvanometer serving as zero instrument with

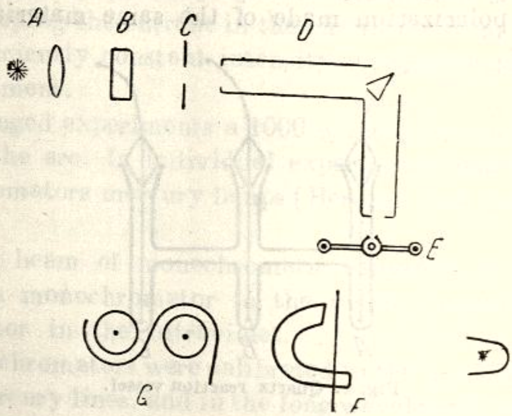

Fig. 2. Scheme of experimental set-up.

its string set in the zero position. The oscillograph set-up was then switched on. By means of the shutter the test electrode was illuminated by a flash of light of the desired wavelength from the optical ystem (Fig. 2). The photogalvanic change in potential, causing a deviation of the galvanometer thread was registered at that moment on the oscillograph film or observed visually.

In this manner the following measurements were carried out:

1. At a given constant value of the current intensity, the photogalvanic effect was measured as a function of the quantity of electricity passed through the test electrode and the accompanying change in the electrode potential.

2. At a constant potential of the test electrode the photogalvanic effect was measured as a function of the wavelength of the radiation.

Experimental results

1. Dependence of the photogalvanic effect on a gold electrode on the quantity of electricity passed and on the accompanying variation of the electrode potential

Figs. 3 and 4 represent the results of two typical experiments. Curve *1* is the charging curve of a gold electrode in 1N sulphuric acid solution. The black dots mark the corresponding photogalvanic effect on the same electrode. On the abscissae axis is plotted the polarization time in minutes and the corresponding quantity of electricity passed through the electrode in microcoulombs. On the ordinate axis—the potential of the test electrode in volts against the potential of the reference electrode in the same solution and the values of the photogalvanic effect: in millivolts in Fig. 3 and in 10^{-5} V in Fig. 4.

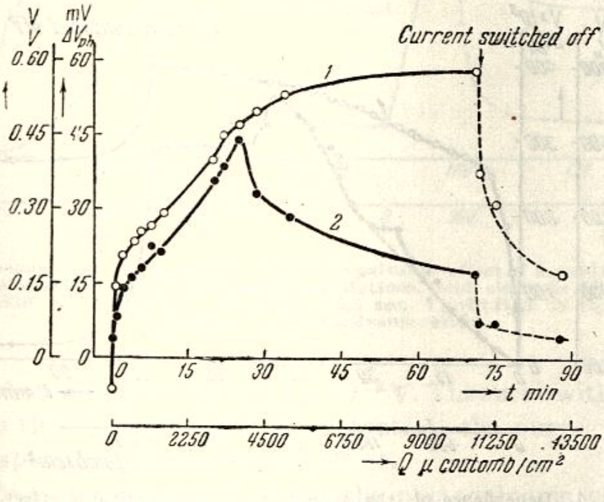

Fig. 3. Dependence of the potential and photogalvanic effect of a gold electrode in 1 N H_2SO_4 on the polarization (white light). *1*, electrode potential; *2*, photogalvanic effect. Gold electrode ($S=1$ cm²) in 1 N H_2SO_4; $I=2.5$ μA; light from a carbon arc; water filter; $V_0 \rightarrow$ Au 1 N H_2SO_4 exposition 1 sec.

The principal difference between these experiments is that in the first case we used a beam of undispersed light of considerable intensity, whereas in the second we used monochromatic light.

The initial potential of a gold electrode which was mechanically cleaned and was in contact with air is usually about $V_H=0.6$ V.

The surface of such an electrode, as follows from the above-cited paper by Deborin and Ershler and from our measurements, is covered with an oxygen film of the order of a monolayer. At this value of the potential the photogalvanic effect of the gold electrode is extremely small.

The charging curve of the gold electrode has three characteristic sections. The rapid rise in the electrode potential immediately after the polarization current has been started corresponds to the formation and polarization of the ionic double layer. The subsequent gentle slope of the curve corresponds to the formation of an oxygen film on the gold electrode. The third horizontal section of the curve corresponds to a steady process on the electrode in which electricity is taken up without change in the potential. Besides the evolution of oxygen in this range higher auric oxides may also be formed here.

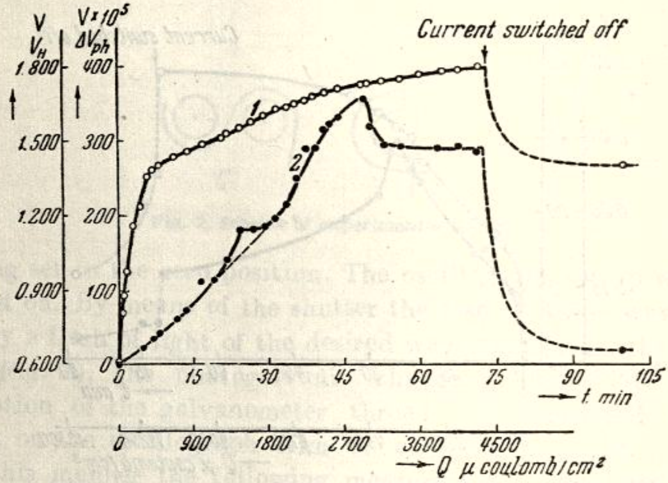

Fig. 4. Dependence of the potential and photogalvanic effect of a gold electrode in 1 N H_2SO_4 on the polarization (monochromatic light). Gold electrode ($S=1$ cm^2) in 1 N H_2SO_4; $\lambda=5520$ Å; $I=1$ μA; exposition 0.5 sec; energy of incident radiation 124×10^{-4} joules; $V_0 \rightarrow Pt/H_2$. 1 N H_2SO_4. *1*, electrode potential; *2*, photogalvanic effect.

In the first two sections of the charging curve the photopotential shows a continuous growth (curve with dots, Figs. 3 and 4) which reaches a maximum when the curve goes over into the range of the steady process, and then falls off sharply.

As was pointed out in our previous paper the observed increase in the photogalvanic effect upon polarization of the electrode can be due both to a thickening of the absorbing oxide layer on the electrode and to the change in the electrode potential.

To separate these two possible causes, we carried out experiments in which a gold electrode was repeatedly polarized, simultaneous measurements being made of the photogalvanic effect.

The results of the measurements are represented in Fig. 5. On the abscissae axis is plotted the polarization time in minutes and for each polarization separately the quantity of electricity passed in microcoulombs, on the ordinate axis the electrode potential

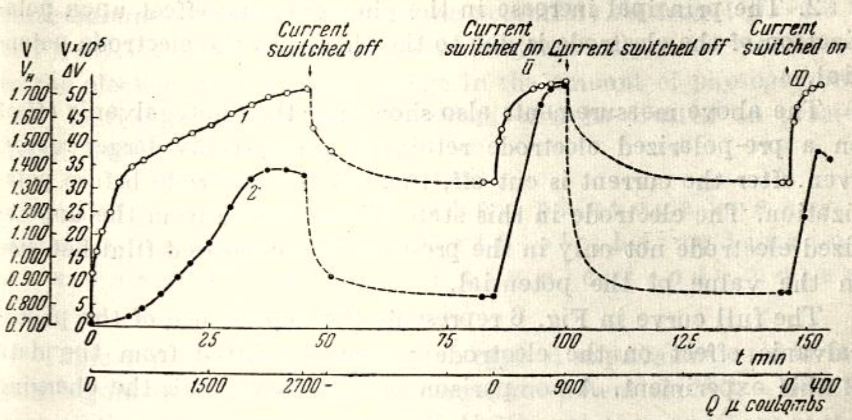

Fig. 5. Dependence of the potential and photogalvanic effect of a gold electrode on the quantity of electricity passed in repeated polarizations. Gold electrode ($S=1$ cm²) in 1 N H_2SO_4; $\lambda=5520$ Å; $I=1.1$ μA; exposition 0.5 sec; $V_0 \rightarrow$ Pt H_2.1 N H_2SO_4. *1*, electrode potential; *2*, photogalvanic effect.

and the photogalvanic effect in 1×10^{-5} V. The curve with the circles represents the rise and fall of the potential, the curve with dots—the corresponding photogalvanic effect.

The first charging curve *1* and the photogalvanic effect corresponding to it obtained on a cleaned gold electrode have all the properties described above. After the anodic polarization has been cut off, a sharp drop is observed in the potential and the photogalvanic effect which then remain constant for a sufficiently long time. The oxygen film remains thereby unchanged and can be quantitatively registered by cathodic polarization at potentials below 1.1 V. These measurements are in quantitative agreement with the data of Armstrong, Himsworth and Butler given in the above-cited paper.

Upon a second polarization of the same electrode from which the oxide film has not been removed (II), considerably less electricity is needed to develop a high potential, and the photogalvanic effect runs into correspondingly high values. Subsequent repeated polarizations (III) have the same effect.

Analysis of the results of these experiments permits us to draw two essential conclusions.

1. Due to hysteresis of the deposition and removal of the oxygen film the potential of the electrode can be varied considerably without any essential change of the amount of oxygen on it.

2. The principal increase in the photogalvanic effect upon polarization of the electrode is due to the change in the electrode potential.

The above measurements also show that the photogalvanic effect on a pre-polarized electrode retains a considerably larger value, even after the current is cut off, than on the electrode before polarization. The electrode in this state differs indeed from the unpolarized electrode not only in the presence of a deposited film but also in the value of the potential.

The full curve in Fig. 6 represents the dependence of the photogalvanic effect on the electrode potential plotted from the data of this experiment. A comparison of this curve with the charging

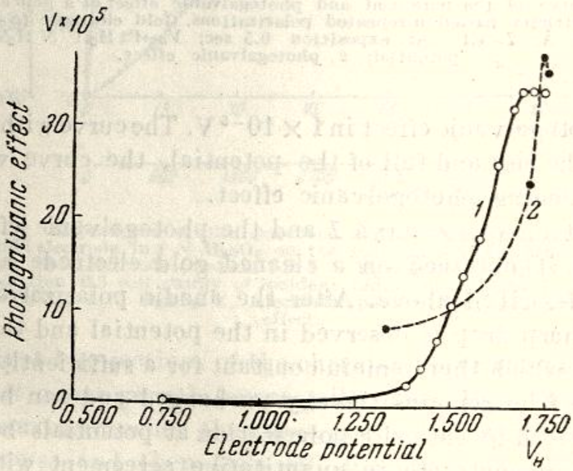

Fig. 6. Dependence of the photogalvanic effect of a gold electrode on the potential. *1*, first polarization; *2*, repeated polarization.

curve (Fig. 5, *1*) shows that the sharp increase in the photogalvanic effect with the rise in potential sets in at a potential $V_H = 1.4$ V at which the oxygen film begins to form and continues up to $V_H = 1.7$ V at which the steady evolution of oxygen commences.

The broken line shows the dependence of the photogalvanic effect on the potential for the same electrode but with a pre-deposited oxygen film (corresponding to curve *III*, Fig. 5).

The mechanism of the influence of the potential on the photogalvanic effect is not discussed here. Despite the small increment in the total amount of oxide as the electrode potential rises from $V_H=1.3$ V to $V_H=1.7$ V there may take place simultaneously with the change in the electric field a sharp change in the amount of photogalvanically active substance. This problem will be treated in greater detail below.

2. Dependence of the photogalvanic effect on the wavelength of the radiation at a constant value of the electrode potential

Table 1 presents the results of a typical experiment carried out with a gold electrode which was charged to a potential of $V_H=1.675$ V by anodic polarization in a 0.1 N H_2SO_4 solution and kept at this potential throughout the experiment.

Table 1

Gold electrode ($S=1$ cm²) in 1 N H_2SO_4; $V_H=1.675$ V; exposition 0.5 sec; $V_0=Pt/H_2 \cdot 1N$ H_2SO_4

λ — Å	Energy of incident radiation joules×10⁴	Photogalvanic effect ΔV V×10⁵	ΔV referred to same energy	ΔV referred to same number of quanta
6840	220	16	5.2	4.1
6120	136	68	36	32
5520	72	148	148	148
4780	29	156	390	450
4420	18	120	480	600
4120	16	124	564	750
3700	12	100	588	870

The Table also gives the absolute values of the energy of the monochromatic radiation falling on the test electrode as measured by a vacuum thermopile with a quartz window.

A Hefner lamp served as a standard. The source of the radiation was an electric arc with a sufficiently steady (throughout the experiment) regime. Filtration and monochromatization were carried out by the method described above. The time of exposition was 0.5 sec for all the wavelengths.

Fig. 7 depicts the results of the measurements given in Table 1. The abscissae are the wavelengths in angströms and the corresponding energies in electron volts. The ordinates are the values of the photogalvanic effect in 1×10^{-4} V and the amount of radiation falling on the electrode in 1×10^{-4} joule.

Curve *I* is the graph of the experimental values of the photogalvanic effect for the corresponding wavelengths.

Curve *II* was obtained by plotting the absolute values of the radiant energy falling on the electrode.

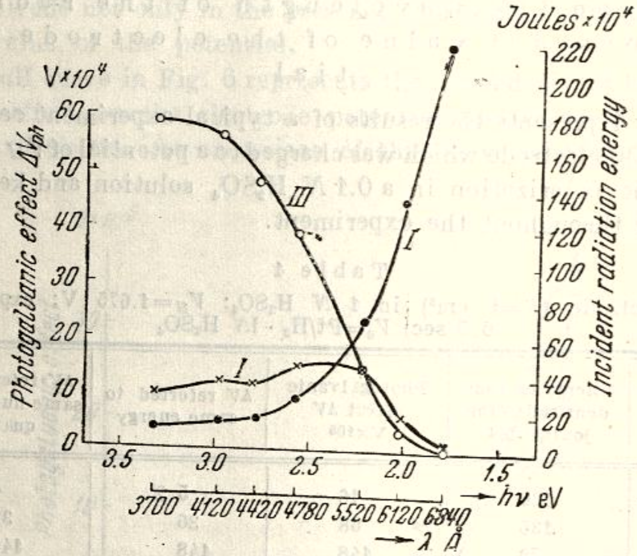

Fig. 7. Spectral sensitivity of the photogalvanic effect of a gold electrode in $1\ N\ H_2SO_4$. *I*, experimental values of photogalvanic effect; *II*, quantities of incident energy; *III*, values of photogalvanic effect referred to the same energy.

Curve *III* gives the values of the photogalvanic effect referred to a spectrum with equal energies. This was done by dividing the magnitude of the measured effect by the corresponding relative value of the radiant energy incident on the electrode.

The amount of incident energy for $\lambda = 5520$ Å is taken as unity.

As appears from Fig. 7 the magnitude of the photogalvanic effect on a gold electrode in $1\ N\ H_2SO_4$ and at a potential of 1.68 V falls off sharply in the wavelength range around 5000 Å. At $\lambda = 5130$Å the energy of a corresponding quantum is 2.4 V and the curve depicting the relative increase in the photogalvanic effect has a sharply defined maximum. However, the electrode retains a noticeable photogalvanic sensitivity up to $\lambda = 6840$ Å.

3. Dependence of the photogalvanic effect on the intensity of the radiation

In order to justify our method of transposing the values of the photogalvanic effect to a spectrum of equal energies it was necessary to check up whether the effect depended linearly on the intensity of the radiation employed. To establish such a relation for the object would be of interest in itself. With this aim we carried out special experiments on a gold electrode in 1 N H_2SO_4 solution. The results of the measurements are given in Table 2 and depicted graphically in Fig. 8.

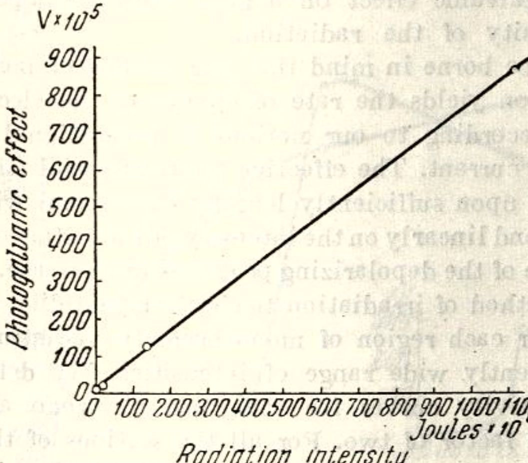

Fig. 8. Dependence of the photogalvanic effect on the intensity of radiation.

The source of the radiation was an incandescent lamp with steady regime. The intensity was varied by regulating the distance from the lamp to the irradiated object. To remove the undesirable spectral region the light was first passed through a 10 cm water filter and a special filter for red light.

The quantity of incident energy was measured by a thermopile whose readings were preliminarily checked for linearity in the given

Table 2

Gold electrode $S=1$ cm² in 1 N H_2SO_4 solution, $V_H=$ $=1.690$ V; exposition 1 sec; source of radiation 1000 W tungsten lamp; filter: 10 cm water+filter cutting off red light

Incident energy joules$\times 10^4$	Photogalvanic effect $V \times 10^5$	Relative coefficient of radiation	Relative photogalvanic effect
6	4	0.52	0.44
11.5	9	1.00	1.00
23	17	2.00	1.89
140	124	12.2	13.8
1100	880	95.6	97.8

range of intensities. The results obtained lead to the unambiguous conclusion that in the measured range of intensities the magnitude of the photogalvanic effect on a gold electrode depends linearly on the intensity of the radiation.

It should be borne in mind that our method of measuring with short exposition yields the rate of change of the electrode potential, which according to our notions is proportional to the true photogalvanic current. The effective photopotential (the maximum value reached upon sufficiently lengthy exposition) will most probably not depend linearly on the intensity of the radiation, due to the great influence of the depolarizing processes in this case. It was difficult by our method of irradiation to check the validity of the linear dependence for each region of monochromatic radiation separately over a sufficiently wide range of intensities. We determined the spectral sensitivity curves for the same electrode at intensities differing by a factor of two. For all the sections of the curve the ratio of the corresponding values of the photogalvanic effect was the same and equal to 2 with an accuracy of 3—4%.

A straightforward experiment was undertaken to clarify the role of thermal radiation. A gold electrode in 1 N sulphuric acid solution was first polarized anodically (about 3000 micro coulombs of electricity per cm² were sent through) and then irradiated by the undispersed light of a 1000 W lamp, once with a water filter to absorb the thermal radiation and a second time without filter. The same beam of light was then allowed to fall on a thermopile. The exposition was 0.5 sec in both cases.

The photogalvanic effect without filter was by four per cent greater than with it, whereas the thermopile showed a threefold increase in the total energy of radiation without the filter. This experiment irrefutably proves that the photogalvanic effect does not depend upon the total quantity of heat communicated.

4. Additional experiments on the photogalvanic effect on a gold electrode

In addition to the principal measurements of the photogalvanic effect on a gold electrode in a 1 N sulphuric acid solution, experiments were also carried out to study the main laws of the effect in a neutral solution of 1 N KNO_3. The experimental method was the same as described above.

Fig. 9 sets forth the results of the measurements of the photogalvanic effect on a gold electrode in 1 N KNO_3 solution as a func-

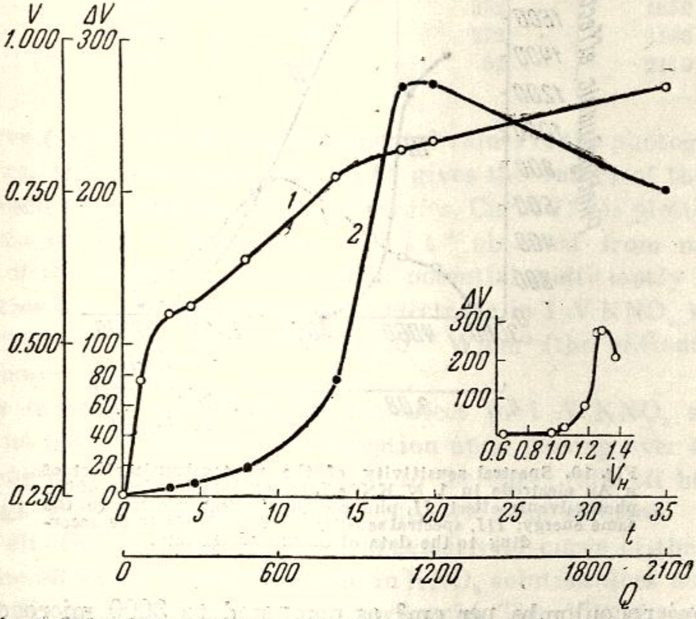

Fig. 9. Dependence of the potential and the photogalvanic effect of a gold electrode in 1 N KNO_3 on the polarization. Gold electrode (S=1cm²) in 1 N KNO_3; λ= 5520 Å; I = 1 μA; $V_0 \rightarrow Pt/H_2 \cdot 1\ N\ KNO_3$; exposition 0.5 sec; energy of incident radiation = 124×10^{-4} joules. *1*, electrode potential; *2*, photogalvanic effect.

tion of the amount of electricity passed, and the corresponding change in the electrode potential. The curve with circles is the charging curve, with dots—the corresponding photogalvanic effect. The coordinates have the same meaning as before. The insert gives the photogalvanic effect as a function of the electrode potential.

Attention is drawn to two characteristic differences between the curve obtained in 1 N KNO_3 and that for the same processes in 1 N H_2SO_4.

1. The maximum of the photogalvanic effect corresponding to the complete formation of an oxide film on the electrode sets in at a considerably lower value of the quantity of electricity, about

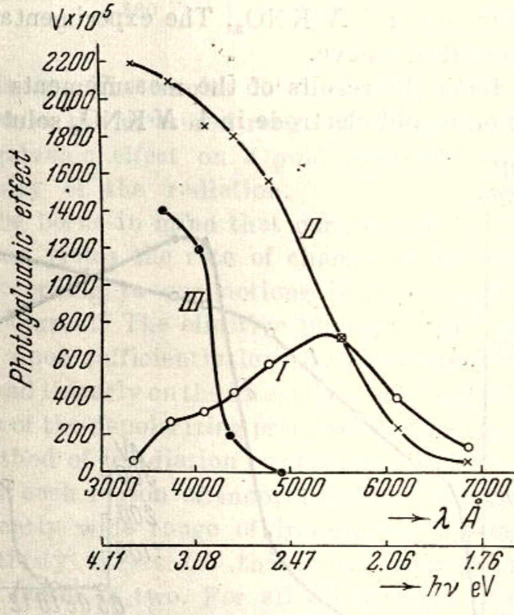

Fig. 10. Spectral sensitivity of the photogalvanic effect of a Au electrode in 1 N KNO_3. *I*, experimental values of the photogalvanic effect; *II*, photogalvanic effect referred to the same energy; *III*, spectral sensitivity of a gold electrode according to the data of Clark and Garrett.

1000 microcoulombs per cm^2 as compared to 3000 microcoulombs in sulphuric acid.

2. The electrode potential (with respect to the normal hydrogen electrode) at which the sharp increase in the effect begins is at a lower value of $V_H=1.0$ V (the corresponding value for sulphuric acid is $V_H=1.4$ V).

It can thus be concluded that in 1 N KNO_3 a photogalvanically active surface is formed at more cathodic potentials and the accompanying oxide film is much thinner.

Table 3 and Fig. 10 set forth the data on the spectral sensitivity of a gold electrode in 1 N KNO_3 at $V_H = 1.4$ V.

Table 3

Gold electrode ($S = 1$ cm²) in 1 N KNO_3; $I = 1 \mu A$; exposition 0.5 sec; $V = 0.995$ V; $V_0 \rightarrow Pt/H_2 \cdot 1\ N\ KNO_3$

λ—Å	Incident energy joules×10⁴	Photogalvanic effect ΔV V×10⁵	ΔV referred to the same energy
6840	292	140	58
6120	218	400	229
5520	124	720	720
4780	46	580	1570
4420	30	432	1800
4120	23	332	1850
3700	16	272	2100
3380	3	52	2180

Curve *I* is the plot of the experimental values of the photogalvanic effect *vs.* the wavelength. Curve *II* gives the values of the effect transposed to a spectrum of equal energies. Curve *III* is plotted from the data of Clark and Garrett[8] obtained from measurements of the effective photogalvanic potential (sufficiently lengthy expositions) on an unpolarized gold electrode in 1 N KNO_3 solution at an intensity of radiation of 4×10^{-4} W/cm² (the ordinate scale is increased tenfold).

The trend of the photogalvanic effect in 1 N KNO_3 solution shows no marked tendency to saturation upon passing over to short wavelengths. The relative increment in the effect falls off here too, although less sharply than in the sulphuric acid solution.

In all other respects the spectral sensitivity curve of the photogalvanic effect on a gold electrode in KNO_3 solution does not differ essentially from the curve in sulphuric acid. The shift of our curves relative to the curve of Clark and Garrett in the direction of long wavelengths can be attributed to the high value of the electrode potential at which our measurements were carried out.

[8] Clark and Garrett, J. Am. Chem. Soc., 61, 1805 (1939).

Preliminary determinations of the photogalvanic effect on an anodically polarized gold electrode in alkaline solution showed that the effect in 1 N KOH is a few hundredth part of the value obtained with the same electrode in H_2SO_4 solution, and quantitative measurements by our method were impossible.

In explaining the observed effect it must be taken into account that the potential of an anodically polarized electrode in alkali differs considerably (up to 1 V) from that of an anodically polarized electrode in acid.

In conclusion we set forth the results of measurements made to determine the dependence of the effective photogalvanic current and the effective photogalvanic potential on the polarizing current density in the region of oxygen overvoltage (Table 4).

The measurements were carried out in monochromatic light of constant intensity. In measuring the effective photogalvanic current the electrode potential ($V_{\mathbf{dark}}$) was kept constant; in measuring the effective photogalvanic potential, the current intentsity ($I_{\mathbf{dark}}$) was kept constant. The measurements were commenced with large current densities and gradually proceeded to smaller values.

Table 4

Gold electrode ($S=1$ cm²) in 1 N H_2SO_4; $\lambda=5200$ Å, $V_0 \rightarrow Pt/H_2$. 1 N H_2SO_4

I_{dark} A×10⁸	V_{dark}, Volt	I_{light} A×10⁸	V_{light}, Volt	ΔV_l mV	ΔI A×10⁻⁸	$\Delta I_l=\frac{I_d \Delta V_l}{0.050}$ A×10⁸
25	1.5920	27.5	1.5838	8.2	2.5	4.1
50	1.6704	53.5	1.6622	8.2	3.5	8.2
100	1.7155	104.5	1.7127	2.8	4.5	5.6
250	1.7682	257.0	1.7671	1.1	7.0	5.5
500	1.7793	510.5	1.7781	1.2	10.5	12.0
Gold electrode ($S=1$ cm²) in 1 N KNO_3; $\lambda=5200$ Å; $V_0 \rightarrow Pt/H_2$. 1 N KNO						
25	0.8556	26	0.8488	6.8	1.0	3.4
50	0.8832	52	0.8844	4.8	2.0	4.8
100	0.9108	102.5	0.9096	1.2	2.5	2.4
250	0.9114	256.5	0.9408	0.6	6.5	3.0
500	0.9637	511	0.9632	0.5	11.0	5.0

With an increase in the polarizing current density the effective photogalvanic current increases and at the same time the increment in the effective photogalvanic potential decreases. The effective photogalvanic current gives a qualitatively correct representation of the dependence of the photogalvanic effect on the potential as obtained by our main method. As has been shown by us elsewhere[1], the effective photogalvanic potential is not a direct measure of the photogalvanic effect and is determined by the total expenditure of electricity in the various processes taking place at the electrode.

Let us try to establish a relation between the effective values obtained for the photogalvanic effect, the total current flowing through the electrode and the true photogalvanic current.

Upon irradiation of the electrode at a constant current I_d in the circuit, the potential of the electrode changes from V_d to V_l. In the region of oxygen overvoltage, when a steady process has set in, the electrochemical discharge current should be equal to

$$I_l = I_d e^{3(V_l - V_d)}.$$

The observed current is the sum of the electrochemical discharge current and the photogalvanic current ΔI_l. At constant current in the circuit we have:

$$I_d = I_l + \Delta I_l$$

whence

$$\Delta I_l = I_d - I_l = I_d - I_d e^{3(V_l - V_d)},$$

i. e. the photogalvanic current is equal to the difference between the light and dark electrochemical discharge currents. If the current in the circuit is constant then until a steady process sets in the photogalvanic current will be expended on the change in the electrode potential and on the compensation of the varying electrochemical discharge current:

$$\Delta I_l = C\frac{dV}{dt} + I_d - I_d e^{3(V - V_d)},$$

where C is the capacity of the electrode, t — the time.

In the first moment of irradiation, $V \to V_d$ the photogalvanic current is $\Delta I_t = C\frac{dV}{dt}_{t\to 0}$ and we obtain the equation formerly derived from the oscillographic curves of the effect [1].

In a steady process $\frac{dV}{dt}=0$. Then:

$$\Delta I_l = I_d - I_d e^{\beta(V_l - V_d)} = I_d\left(1 - e^{\beta(V_l - V_d)}\right).$$

On the basis of Bowden's [9] data on oxygen overvoltage we take $\frac{1}{\beta}=0.050$ and can then compute the absolute values of the photogalvanic current at different polarization currents from the values of the effective photogalvanic change in the potential.

Taking for the effective photogalvanic potential $V_l - V_d = -\Delta V_l$ we obtain for small values of ΔV_l:

$$\Delta I_l = I_d\left(1 - e^{\frac{V_l - V_d}{0.050}}\right) = I_d \frac{\Delta V_l}{0.050}\ .$$

The last column of Table 4 gives the values of ΔI_l calculated by this formula.

Considering the difficulties involved in accurately measuring the effective photovoltaic effect (lengthy exposition), the agreement obtained between the computed values of ΔI_l and the experimentally measured increment of the current ΔI at constant potential and irradiation of the electrode in sulphuric acid is satisfactory. The discrepancy between the computed and measured values of ΔI_l in the neutral KNO_3 solution is probably due to the unsteady character of the process.

From the absolute value of the photogalvanic current and from the rate of change of the photogalvanic potential measured by our main method, one can compute sufficiently accurately the capacity of the electrode

$$C = \frac{\Delta I_l}{dV/dt_{t\to 0}} = \frac{I_d\left(1 - e^{\frac{V_l - V_d}{0.050}}\right)}{dV/dt_{t\to 0}}.$$

For the measurements depicted in Fig. 4 at an effective value $\Delta V_l = 22.4$ mV we have $-\frac{dV}{dt}=5.7$ mV/sec; $I_d = 1\times 10^{-6}$ A. Hence the capacity of the electrode for this potential range ($V_H = 1.8$) is approximately equal to 100 μF.

The preceding discussion also explains why despite the linear dependence of the true photogalvanic current on the intensity of

[9] Bowden, Proc. Roy. Soc., A **126**, 107 (1930).

the radiation a linear dependence will be observed for the effective photogalvanic increment in the potential only at small values of ΔV_l; at large values of ΔV_l the dependence on the intensity will be logarithmic.

Adler[10] applied the method of the transitional state to the investigation of a steady photogalvanic process balanced by diffusion and established a similar relation between ΔV_l and the intensity of the radiation.

5. The spectral sensitivity of the photogalvanic process on a gold electrode as a function of the electrode potential

It is of considerable interest for an interpretation of the mechanism of the photogalvanic effect to establish the dependence of the magnitude and red boundary of the effect on the electrode potential.

The occurrence of hysteresis in the removal of the oxygen film on a gold electrode in sulphuric acid solutions made it possible with sufficient approximation to obtain an electrode whose potential could be varied over a considerable range (1.7—1.3 V) without any marked disturbance of the amount of surface oxide film. We shall not consider here the possible mechanism of thus varying the potential. In case the variation of the electrode potential reduces merely to a change in the electric field, without affecting the quantity of photogalvanically active substance, it becomes possible with such an electrode to establish the influence of the electric field on the photogalvanic process.

Before the measurements, the electrode was charged to a high potential and after formation of an oxide film, a curve of spectral sensitivity was obtained.

Fig. 11 represents graphically the results of one of the typical measurements. The abscissae are the wavelengths of the applied radiation in angströms and the corresponding energy in electron volts. The ordinates are the values of the photogalvanic effect in 1×10^{-4} V, referred to a spectrum of an equal number of quanta; the number of quanta of monochromatic radiation at $\lambda = 5520$ Å being taken for unity.

---

[10] E. Adler, J. Chem. Phys., 8, 500 (1940).

Curve I was obtained at an electrode potential $V_H=1.716$ V. Curve II for the same electrode corresponds to $V_H=1.500$ V. The intensity of the radiation and the entire method of measurement were strictly the same for both curves.

On the basis of the results obtained from the above experiment and from a whole series of similar measurements we can formulate the following sufficiently well satisfied relation: In order to keep the value of the true photogalvanic current constant near the red boundary, when the electrode potential is increased by a given

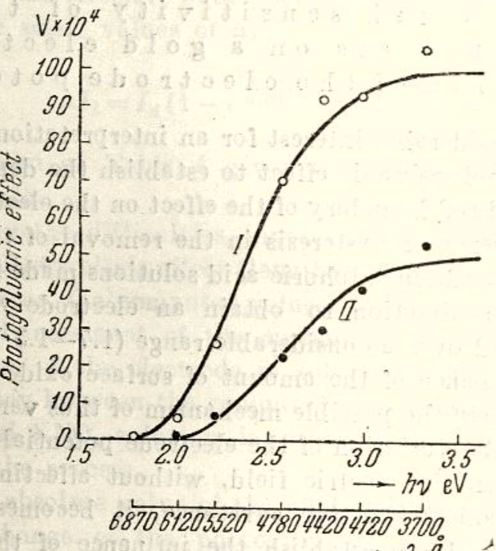

Fig. 11. Dependence of the spectral sensitivity of the photogalvanic effect of a gold electrode on the potential. I, $V_H=1.716$ V; II, $V_H=1.500$ V.

amount the energy of the quanta of the radiation applied must be reduced by the same amount.

Indeed, in the above experiment the difference between the electrode potentials in the first and second runs was 0.216 V. The difference between the energies of the radiation in electron-volts, giving the same photogalvanic effect in both cases, was 0.200—0.220 in the region of minimum measured values of the effect. If the difficulty of making measurements in this region is taken into account, it must be conceded that the above formulated relation is sufficiently well borne out.

This relation, approximately true for a gold electrode, may be written as follows:

at $I_1 = I_2$

$$\varepsilon(V_1 - V_2) = h(\nu_2 - \nu_1) \quad \text{or} \quad V_1 - V_2 = \frac{h}{\varepsilon}(\nu_2 - \nu_1),$$

where I, V and ν are, respectively, the photogalvanic current, potential and frequency of the radiation for the first and second electrodes.

However, at sufficiently large values of the quanta this condition is not fulfilled. As appears from Fig. 11, the limiting value of the photogalvanic effect varies, being smaller the lower the electrode potential. Evidently the complete influence of the electrode potential on the photogalvanic effect is not limited to the change of the electric field at the surface.

Mechanism of the photogalvanic process on a gold electrode

Our curves giving the photogalvanic effect on a gold electrode as a function of the quantity of electricity passed and the data of the above cited work of Bose and Kochan allow us to conclude unambiguously that the photogalvanically active material in the process is the surface compound of gold with oxygen which forms upon anodic polarization of the electrode.

From the experimental relations obtained it is difficult to determine the electrical state of the adsorbed photogalvanically active material, *viz.*, the extent to which it differs from the oxygen ion, or to decide whether the entire or only part of the oxygen film formed is photogalvanically active.

In studying the external photoelectric effect a number of authors established that an oxygen film on a gold electrode increases the work function of the electron; in other words the oxygen film creates an additional negative potential on the outer surface of the metal[11].

If, in addition, it is taken into consideration that the electrode in our experiments was at strongly positive values of the potential, then the reversal of the sign of the effect in the photogalvanic process with respect to the photoelectric process appears quite regular.

---

[11] Whalley and Rideal, Proc. Roy. Soc., A, **140**, 484 (1933).

A light quantum acting on negatively charged photogalvanically active material in the strong electric field of the electrode, tears off the electrons absorbed by the metal and leads to the evolution of free atomic oxygen. The energy of the quantum in the range of the main increase of the photogalvanic effect on a gold electrode ($h\nu \cong 2.5$ electron-volts) is of the order of the dissociation energy of an oxygen molecule. The photo nic process evidently proceeds by a less profitable reaction than the purely electrochemical evolution of oxygen.

The absolute value of the energy of the photogalvanic process which depends on the electrode potential must thus be considered as including in addition to the energy of the reacting system a constant characterizing the height of the potential barrier (activation energy) of the process.

Consider the spectral sensitivity curve of the photogalvanic effect of a gold electrode on the basis of the proposed scheme of the process. Table 5 and Fig. 12 represent the data of one of the characteristic experiments.

Table 5

Gold electrode ($S=1$ cm^2) in 1 N H_2SO_4 solution; $I=0.2\mu A$; $V_H=1.680$ V; quartz monochromator, slit 0.5 mm; exposition 0.5 sec; $V_0 \rightarrow Pt/H_2 \cdot 1\ N\ H_2SO_4$

λ in Å	Energy of incident radiation joules×10⁴	Photogalvanic effect ΔV V×10⁵	ΔV referred to same energy	ΔV referred to same number of quanta	Remarks
6840	86	3.0	0.7	0.56	Filter cuts off red region
6120	16	5.0	6.3	5.6	
5520	20	27.0	27.0	27.0	
4780	16	68	85.0	98.0	
4420	8.6	42.0	98.0	122.0	
4120	1.45	7.5	103.0	137.0	Black filter letting through near ultra-violet
3700	3.6	17.0	94.5	140.0	
3380	1.25	7.0	111.0	180.0	

The dots denote the experimental values of the photogalvanic effect referred to the same number of incident light quanta; the broken line represents the relative increase in the photogalvanic effect with variation of the energy of radiation and hence characterizes the amount of photogalvanically active matter which reacted under the influence of the same number of quanta of different energy.

In general, this curve characterizes the probability of the photogalvanic process which depends both on the distribution in energy of the photogalvanically active complexes and on the probability of reaction of a complex possessing sufficient energy.

If it is assumed that the probability of reaction is constant in a given energy interval for complexes with sufficient energy, then the broken line in Fig. 12 characterizes the energy distribution

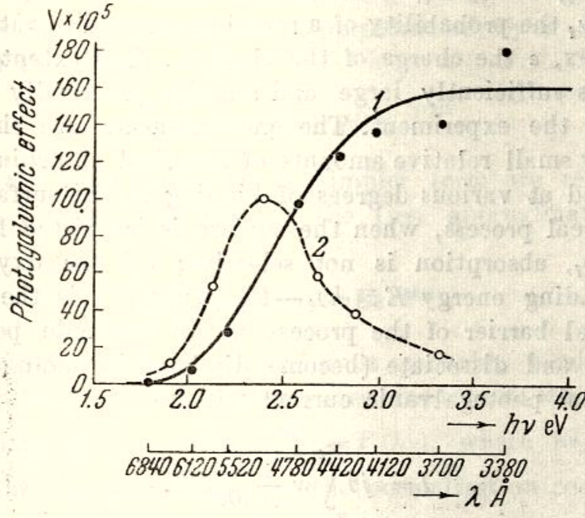

Fig. 12. Dependence of the spectral sensitivity of the photogalvanic effect of a gold electrode on the energy of the incident radiation quantum. *1*, photogalvanic effect referred to the same number of quanta; *2*, relative increment in the magnitude of the photogalvanic effect.

of photogalvanically active matter. The form of the spectral sensitivity curve of the photogalvanic effect on a gold electrode forces us in this case to assume a nonhomogeneous distribution in energy of the reacting complexes. By our scheme of the process such an inhomogeneity in the energy distribution corresponds to different binding energies of the adsorbed complexes with gold, which can be most naturally explained by the inhomogeneity of the electrode surface. The above scheme of the photogalvanic process can be described in the first approximation by the following equations:

The photogalvanic current due to dissociation of absorbing complexes of the i-th kind with binding energy E_i corresponding to a quantum $h\nu_i$ and with selective absorption will be

$$I_i = \varepsilon j \theta w_i \frac{N_i}{N},$$

where I is the current intensity, j the intensity of irradiation expressed in the number of quanta falling on the electrode per second, θ the extent of surface covered by photogalvanically active complexes at a given electrode potential, N_i the number of complexes with binding energy E_i, N the total number of complexes on the electrode, w_i the probability of a reaction when a quantum strikes an i-complex, ε the charge of the electron. The extent of surface covered θ is sufficiently large and remains practically unchanged throughout the experiment. The measurements are thus carried out at very small relative amounts of adsorbed absorbing complex removed and at various degrees of binding to the surface.

In the real process, when the surface is irradiated by light of frequency ν_i, absorption is not selective; all the oxygen atoms with a binding energy $E \lesseqgtr h\nu_i - U_v$ (where U_v is the energy of the potential barrier of the process at an electrode potential V) can absorb and dissociate (become discharged) photogalvanically and the total photogalvanic current will be

$$I = \varepsilon j \theta \int_{E_0}^{E_i} w \frac{1}{N} \frac{\partial N}{\partial E} dE.$$

In order to take this integral in the general case, it is necessary to know not only the distribution in binding energy of the absorbing complexes but also the dependence of the probability of reaction of the absorbing complex w on the binding energy and on the energy of the quantum of radiation.

Substituting conditionally for the probability of the reaction w a constant value for the given energy interval $\overline{w}$ and observing that in our experiments in the proposed scheme of the process we have $\frac{dI}{dE} = \frac{dI}{d(h\nu)}$, there obtains:

$$I = \varepsilon j \theta \overline{w} \int \frac{1}{N} \frac{\partial N}{\partial E} dE = A' \int \frac{1}{N} \frac{\partial N}{\partial E} dE$$

whence

$$\frac{dI}{d(h\nu)} = \frac{dI}{dE} = A' \frac{1}{N} \frac{\partial N}{\partial E} = A' \varphi(E).$$

Thus, under the above assumption, the derivative of the experimentally established relation between the photocurrent and the energy of the quantum of radiation gives the curve of the distribution of the adsorbed absorbing complex with respect to the energy of binding to the surface with an accuracy up to a constant factor.

Carrying out a graphical differentiation of the experimental relation $I = f(h\nu)$ we obtain $\frac{dI}{d(h\nu)} = f'(h\nu)$. The resulting curve, represented in Fig. 12 is well approximated by a distribution function of the form:

$$\frac{1}{N} \frac{\partial N}{\partial E} = \varphi(E) = aE^2 e^{-\beta^2 E^2}.$$

To obtain the final results in a simpler form we represent the experimental curve obtained in the first approximation by the function

$$\frac{1}{N} \frac{\partial N}{\partial E} = \varphi(E) = aEe^{-\beta^2 E^2}.$$

The quantity $1/\beta$ is here the most probable binding energy of the absorbing complex and is determined from the position of the maximum of the curve $\frac{dI}{d(h\nu)} = f'(h\nu)$, where $h\nu_m = \frac{1}{\beta} + U_\nu$. The constant a is determined by the normalization condition:

$$\int_0^\infty aEe^{-\beta^2 E^2}\, dE = 1; \quad \text{whence } a = 2\beta^2.$$

Thus, in principle, photovoltaic measurements furnish a method of establishing the true picture of the energy state of adsorbed photogalvanically active complexes (oxygen on gold in our case) if the value of w which we conditionally took for a constant, is found.

In the proposed scheme of the mechanism of the process, we have

$$I = \varepsilon j \theta \overline{w} \int_{E_0}^{E_i} \frac{1}{N} \frac{\partial N}{\partial E}\, dE = \varepsilon j \theta \overline{w} a \int_{E_0}^{E_i} Ee^{-\beta^2 E^2}\, dE.$$

After integration and some simplifying transformations we obtain

$$I = \varepsilon j \theta \overline{w} e^{-\beta^2 E^2} \Big|_{E_i}^{E_0}.$$

From the dependence of the energy of the process on the electrode potential considered above it follows that for the realization of an elementary photovoltaic act at an electrode potential V it is necessary to expend the energy:

$$Q = E + U_v = E + U_{v_0} - \alpha\varepsilon\Delta V \gtreqless h\nu,$$

where U_{v_0} is the energy of the potential barrier at $V = V_0$ and $\Delta V = V - V_0$. The factor α can be represented as the product of two coefficients determining the part of the effective potential and the effective charge of the reacting complex. This quantity will be more fully specified below.

With a change in the electrode potential the value of θ in the general case also changes. For the range of potentials under investigation we shall take a linear relation:

$$\theta_v = \theta_0 + \gamma'\Delta V = \theta_0(1 + \gamma\Delta V),$$

where θ_0 is the extent of surface covering by photovoltaically active complexes at $V = V_0$. It is now easy to determine the limits of integration in the above expression for the current intensity corresponding to a quantum $h\nu$ and a potential $V - V_0 = \Delta V$.

Since by definition the integral should give all the absorbing complexes with an energy of the process not exceeding the energy of the applied electric field and the incident quantum $E + U_{v_0} \lesseqgtr h\nu + \alpha\varepsilon\Delta V$, the upper limit $E_i = h\nu + \alpha\varepsilon\Delta V - U_{v_0}$, and the lower $E_0 = 0$.

Considering the limits and substituting for θ_v its value we obtain the final expression giving the relation between the photocurrent, the intensity and frequency of the radiation and the electrode potential:

$$I = \varepsilon j \theta_0 (1 + \gamma\Delta V) \overline{w} \left[1 - e^{-\beta^2 (h\nu + \alpha\varepsilon\Delta V - U_{v_0})^2}\right] = \varepsilon j \theta_0 (1 + \gamma\Delta V) \overline{w} L,$$

(L denotes the expression in the brackets). The resulting equation gives the dependence of the photocurrent on the intensity and energy of the radiation, the potential of the electrode and the individual properties of the system characterized by the constants γ, α, θ_0 and U_{v_0}.

Assuming a definite mechanism of the elementary act one can attempt to determine the physical meaning of the quantity U_{v_0} and its relation to the principal energy parameters of the absorbing complex.

In the experiment, the results of which are depicted in Fig. 12, the maximum increment of the photogalvanic effect corresponds to $h\nu_m = 2.4$ electron volts. The character of the increase of the effect (the energy distribution of the absorbing quanta, according

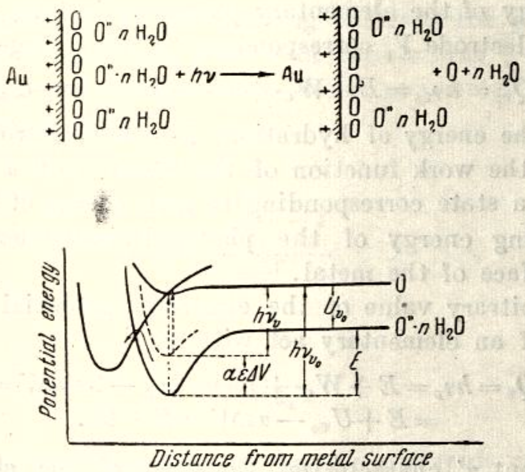

Fig. 13. Schematic representation of an elementary act of the photogalvanic process.

to our representation) corresponds to a value of $\frac{1}{\beta} = 0.7$ eV whence the value of the potential barrier of the process is determined: $U_v = h\nu_m - \frac{1}{\beta} = 1.7$ eV is numerically equal to the energy of the quantum at the red boundary of the photovoltaic effect at an electrode potential $V_H = 1.68$ V; $U_{v_0} = U_v + \alpha\varepsilon\Delta V$.

Fig. 13 schematically represents a possible mechanism of the elementary photogalvanic act and gives the curves of the potential energy of an atom and hydrated oxygen ion with respect to the electrode surface.

The action of a light quantum consists in bringing an oxygen ion into the atomic state under the simultaneous action of the electric field of the electrode surface which captures the excited electrons. The dotted arrows indicate the path of transition of the oxygen from the potential curve of the ion to the potential curve of the atom in a photogalvanic act, in agreement with the Frank-Condon principle. The curved arrow indicates a possible, energetically preferable path of electrochemical discharge of an oxygen ion. The simplest possible scheme of the process $Au^{+}\overline{O}+h\nu\rightarrow$ $\rightarrow Au+O$ though reflecting the essence of the photogalvanic act, does not, however, explain the totality of electrochemical phenomena observed on the electrode.

The energy of the elementary photochemical act Q at a potential of the electrode V_0 corresponding to zero charge will be:

$$Q_{v_0}=h\nu_{v_0}=E+W_{o''}+I_{o''}-2\varepsilon\varphi=E+U_{v_0}.$$

Here W is the energy of hydration, I — the electron affinity of oxygen, $\varepsilon\varphi$ the work function of the electron on a gold surface which is in a state corresponding to zero charge of the electrode, E the binding energy of the photovoltaically active complex with the surface of the metal.

At an arbitrary value of the electrode potential $\Delta V=V-V_0$ the energy of an elementary act will be:

$$Q_v=h\nu_v=E+W_{o''}+I_{o''}-2\varepsilon\varphi-2\alpha'\varepsilon\Delta V=$$
$$=E+U_{v_0}-\alpha\varepsilon\Delta V=E+U_v.$$

The coefficient α' characterizes the part of the change in the potential which affects the photovoltaic process.

At the red boundary of the photovoltaic effect ($E=0$) we obtain:

$$h\nu_0=U_{v_0}-2\alpha'\varepsilon\Delta V=W_{o''}+I_{o''}-2\varepsilon\varphi-2\alpha'\varepsilon\Delta V=$$
$$=W_{o''}+I_{o''}-2\varepsilon(\varphi-\alpha'\Delta V).$$

The equation obtained, despite the insufficient foundation for the proposed mechanism of the process, indicates a possible way of utilizing the data of the spectral sensitivity of the electrode for determining important electrochemical quantities.

Let us consider the final expression for the photogalvanic current

$$I=\varepsilon j\theta_0(1+\gamma\Delta V)\overline{w}L.$$

When the boundary frequency is $h\nu=U_{v_0}-\alpha\varepsilon\Delta V$ the value of L becomes zero. The photogalvanic current is $I=0$. If the parameter

$\beta(h\nu+\varkappa\varepsilon\Delta V-U_{v_0})=3$, then $L=1$ with an accuracy to the fourth significant figure (in the given experiment this condition is fulfilled at $h\nu=3.8$ eV). The photogalvanic current takes on the limiting value

$$I_\infty=\varepsilon j\theta_0(1+\gamma\Delta V)\overline{w}=\varepsilon j\theta_v\overline{w}.$$

This expression defines the physical meaning of $\overline{w}$ as the quantum yield at sufficiently large values of the quanta and $\theta_v=1$.

The determination of the limiting values of the photogalvanic effect at various potentials permits of determining γ and comparing it with the value found from the experimental data on the capacity of the electrode.

Indeed

$$\gamma=\frac{\frac{I_{v\infty}}{I_{v_0\infty}}-1}{\Delta V}$$

whereas

$$\gamma=\frac{C}{q_0\theta_0}.$$

Here I_∞ is the limiting value of the photogalvanis current at the corresponding potential, q_0 the charge of the monomolecular surface layer, C the capacity of the electrode.

For the investigated range of the potentials γ is of the order of 5 reciprocal volts.

It is evident that, if the capacity of the electrode is entirely determined by the process of formation of the photogalvanically active complex, then the preceding relations also allow of establishing the absolute value of θ, the extent of electrode surface covered by the photogalvanically active substance.

In order to determine the absolute value of the quantity $\overline{w}\theta$ and to compare the experimental data with the values of the effect computed by the formula obtained, it must be taken into consideration that the measured photogalvanic effect is

$$\Delta V_{\mathrm{ph}}=\frac{I\Delta t}{C},$$

where C is the capacity of the electrode at the given potential; Δt — the time of exposition. Hence the measured photogalvanic effect at sufficiently small values is:

$$\Delta V_{ph} = \frac{\varepsilon j \theta_v \, \overline{w} \, \Delta t}{C} L.$$

Putting the capacity of the electrode $C = 100 \, \mu F$ and taking from the experiment the limiting value of the effect as 1.6×10^{-3} V we obtain for the conditions of the experiment $\theta \overline{w} = 0.0002$.

In view of the absence of exact data on the capacity of the gold electrode in this range of potentials the value of $\theta \overline{w}$ found characterizes only the order of magnitude of this quantity.

Combining the experimental data and expressing the number of incident quanta per second as $j = \frac{j'}{\varepsilon h\nu}$, where j' is the intensity of radiation in watts and $h\nu$ the energy of a quantum in volts, we obtain:

$$\Delta V_{ph} = A(1 + \gamma \Delta V) \frac{j' \Delta t}{h\nu} [1 - e^{-\beta^2 (h\nu + \alpha\varepsilon \Delta V - U_{v_0})^2}].$$

For the investigated photovoltaic process on a gold electrode the quantity A as determined experimentally is of the order of 2V.

Fig. 11 depicts the dependence of the photogalvanic currents on the frequency of the applied radiation as computed by the derived formula and referred, as are experimental data, to the same number of quanta.

The proposed semi-empirical equation represents a first attempt to establish a relation between the principal characteristics of the photogalvanic process with a consideration of the electrochemical parameters and the state of the electrode surface.

The relationships obtained can be further specified when the true mechanism of an elementary act and the kinetics of the process become known. We believe that interesting material on the nature of the process could be obtained by subjecting the electrode to the action of polarized light. A photogalvanically active surface represents a system of oriented light-sensitive complexes and should possess anisotropic properties and a selective absorption maximum.

Summary

1. A relation has been established between the magnitude of the photogalvanic effect on a gold electrode and the amount of electricity passed, which determines the potential of the electrode and the extent of its covering by an oxygen film.

2. A relation has been established between the photogalvanic effect and the intensity of radiation.

3. The spectral sensitivity of the photogalvanic effect on a gold electrode has been determined.

4. The dependence of the spectral sensitivity on the electrode potential has been established and it is shown to what extent the relation of equivalence between the action of an electric field and the energy of a quantum of radiation is valid in the photogalvanic process studied.

5. A probable mechanism of the photogalvanic process on a gold electrode is discussed and a relation given between the value of the effect, the intensity and frequency of the radiation, the electrode potential and the energy characteristics of the photogalvanically active complex adsorbed on the electrode.

The present investigation was carried out in the laboratory of Prof. A. Frumkin to whom I express my sincere gratitude for his constant attention to the work and valuable advice in its organization and carrying out.

I am also indebted to Prof. A. Terenin for his interest in the work and fruitful discussions.

Karpov Institute of Physical Chemistry,
Moscow.

Received
October 26, 1945.