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Cyrias Ouellet* and Eric K. Rideal, *Laboratory of Colloid Science, Cambridge*
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A photoelectric tube counter of special design has been used for investigating adsorbed layers on a gold surface. The high sensitivity of the counter allows accurate measurements of photoelectric thresholds to be made with continuous ultraviolet light from a source of moderate intensity. The variation of the work function φ with the amount of adsorbed material can thus be followed quantitatively and continuously. The formation of gold oxide layers proceeds over definite steps with increases of 0.35 volt in the work function. The adsorption of iodine is reversible and the resulting increase in the work function varies with the iodine pressure according to a Langmuir isotherm, the saturation value being $\Delta\varphi = +0.21$ volt. The adsorption of ethyl alcohol is also reversible, but gives rise to a double threshold, suggesting the existence of liquid islands on the gold surface.

Introduction

THE effects of gases and vapors both on the intensity and on the threshold of the photoelectric emission of metals have long been recognized as the greatest of the experimental difficulties to be overcome in the measurement of photoelectric thresholds.[1] In spite both of the complexity of the phenomena observed and of the conflicting results obtained it appears clear that a distinction can be made between occluded and adsorbed gases, that the photoemission is affected by external gases only insofar as they are adsorbed on the surface and that an increase in the emission is generally connected with a decrease in the work function and an adsorption of an electropositive gas and *vice versa*. No serious attempt appears to have been made to utilize the photoelectric method for examining the actual behavior of gases and vapors on adsorption as revealed by a change in the photoelectric behavior of the surface.

The extreme sensitivity of a photoelectric counter permits of the evaluation of changes in the photoelectric threshold of metallic surfaces caused by the adsorption of gases or vapors to a high degree of precision $\sim 10A$ with the aid of a relatively weak continuous source of radiation, and at the same time the shape of the photoemission curves in the neighborhood of the threshold can be explored by this means much more accurately than by the usual photoelectric method.

Experimental

The modified type of Geiger-Müller Rajewsky photoelectric counter[2] constructed for these experiments is shown in Fig. 1. It consisted of a Pyrex glass cylinder 20×6 cm provided with a quartz window Q and a Pyrex cap (1 ii). The photon receiver consisted of a cylindrical metal (usually gold) tube C 2 cm long and 1 cm in diameter provided with an axial 2 mm slit for admission of the light. The cylinder C was mounted vertically by a well insulated lead passing through a ground joint plug (a) in the cap. The tungsten anode wire W running down the axis of the metal cylinder was mounted eccentrically on a Pyrex glass frame and connected by well insulated nickel wire to a lead passing through a second ground-glass joint (b) in the cap. By suitable rotation of the plugs (a) and (b) in the cap the wire anode could be inserted along the axis of the photon receiver tube or removed therefrom by passage through the slit. Two fixed leads d and e were used occasionally for heating the metal cylinder and filament. As cathodes metals with thresholds below $\lambda = 3000A$ were used, the Pyrex walls provided adequate screening against stray ultraviolet radiation.

A voltage of some 1000–1500 volts is applied through a 10^9 ohm resistance to the electrodes. When an electron is emitted, on its acceleration by the field through a gas at a few cm pressure in the tube the ionization effected by collision gives rise to a small discharge. The resulting voltage impulse is transmitted through a condenser to the grid of an amplifying valve and

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* Lecturer at the École Supérieure de Chimie, Université Laval, Quebec, Canada.

[1] For a discussion see Gudden *Licht-elektrische Erscheinungen*, Berlin; Hughes and Dubridge *Photo-electric Phenomena*.

[2] Rajewski, Zeits. f. Physik **63**, 570 (1930); Physik. Zeits. **32**, 121 (1931).
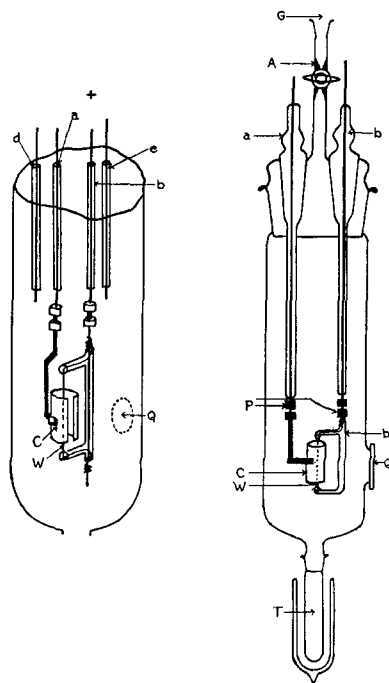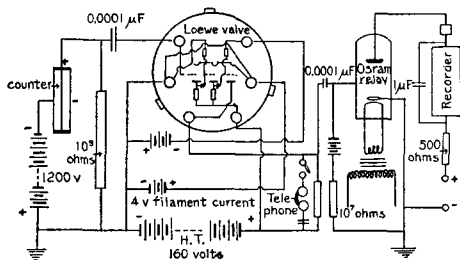
FIG. 1.

FIG. 2.

recorded on a counter in the usual manner and shown diagrammatically in Fig. 2.

Such glass-contained counters exhibit better working characteristics than ones in which ebonite insulation is provided.[3] The counting rate as a function of the voltage was determined both with ultraviolet light and with a weak RaD source; the latter was also used as control before each run. With the radioactive source constant

rates extending over a range of 100–120 volts were easily obtained, whereas with light both the number and size of the impulses were found to increase gradually with the voltage after the sharp initial rise as already noted by Locher.[4] In some cases the voltage plateau consisted of two steps of ranges of about 30 and 100 volts, respectively, with an increase of some 50 percent in the counting rate at the higher potential plateau, a state of affairs apparently favored by the use of light of wavelengths near the threshold; this phenomenon seems to support the view of Locher[4] that electrons with low initial velocities may fail to produce ionization unless they are drawn out by a sufficient field; the presence of steps is thus due to inhomogeneities in the field due either to microscopic cracks or some defect in the geometry of the electrodes. The dark rate in air was found initially to be three per minute; later, due to accumulated radioactive contamination, it rose to a steady value of about 26 per minute, a rate inappreciable to the values obtained when photoelectric measurements were made. As light source a hydrogen lamp consuming 0.3 ampere at 2000 volts was generally employed in conjunction with a Leiss double quartz monochromator. The radiation was found to be uniform in intensity between 3200A, the lowest threshold measured, and 2200A and fell off rapidly at 2100A, the limit of effective transmission of the optical system. Over the range 3200A and 2400A a quartz tungsten filament lamp with a filament temperature of 2800°K was likewise employed. The absence of a marked tail at the foot of the threshold curves shows that the light was sufficiently monochromatic. With an iron arc, very fine slits 0.01 mm could be employed, but it was felt that the sharpness of the thresholds obtained was largely illusory due to the irregular spectral energy distribution and lack of constancy of the source. The counter was connected to a mercury diffusion and Hyvac evacuation system by ground joint connections, a liquid air and cadmium or gold trap being inserted in the line to retain mercury vapor when desired. Oxygen free electrolytic hydrogen and nitrogen and air, the latter purified from dust by passage through olive oil, were stored over phosphoric

[3] Rajewsky, Ann. d. Physik **20**, 13 (1934); Locher, Phys. Rev. **42**, 525 (1932).

[4] Locher, Phys. Rev. **42**, 532 (1932).

anhydride before use. Traces of mercury vapor accidentally introduced into the counter were difficult to remove, filling the bulb with wet oxides of nitrogen for a short time being the most effective method.

In carrying out a run the substance to be adsorbed was introduced into the tube T (Fig. 1) which was then cooled to the temperature of liquid air and the system evacuated. The tube T was then placed in a constant temperature bath to give the desired vapor pressure, and when equilibrium was established the total pressure in the counter was raised to the required pressure for counting by admission of dry gas. The high tension was then applied and the rates of counting with light of a series of wavelengths determined. Counting periods of from one to five minutes, generally one minute, were sufficient. The points on the curves were not determined in their natural sequence but at random, thus rendering any change in the photoelectric behavior of the cathode during the run easily detectable. The chief advantage of the method lies in the high sensitivity of the counter, a beam of only 50 quanta per second falling on the metal could be detected, thus permitting the use of the relatively weak continuous spectrum of hydrogen, very fine slits and a double monochromator. Again, due to the sensitivity of the counter the intensity axis of the threshold curves is greatly elongated and their otherwise asymptotic foot already shows an appreciable slope resulting in a sharper definition of the shape of the foot and of the point at which the curves cut the wavelength axis.

On the other hand, the necessity of using a gas makes it impossible to work with outgassed metals under ideal conditions, and the method is applicable only to systems in which either selective adsorption is predominant or where the vapors may be employed at relatively high pressures. In some cases the possibility of the adsorbed layer being disturbed by the discharge in the counter or by the photons passing through the gas or falling on the surface have to be taken into consideration, e.g., in the presence of the vapor of carbon disulphide. Finally the role of adsorbed films on the wire anode is an all important one for the successful operation of the counter; thus if the gold cathode and wire are

cleaned by a discharge in hydrogen at low pressure and the counter subsequently filled with pure hydrogen or nitrogen, no counting is obtained for some time but only a continuous discharge, an effect also observed by Bosch.[5] On introduction of a mere trace of oxygen counting is resumed immediately.

THE PHOTOELECTRIC BEHAVIOR OF GOLD IN THE COUNTER

As a preliminary to the measurements of the effects of adsorption the photoelectric behavior of gold was first examined. The threshold of thoroughly outgassed gold at 20°C was found by Morris[6] to lie at 2560A ($\phi = 4.83$ volts) and to travel during the process of outgassing from $\sim$ 2100A to 3200A and back to the end value of 2560A a maximum excursion of about 2 volts. For non-outgassed gold Suhrmann and Roy found values of 2597A and 2625A[7] whilst Goetz[8] gives 2800A (4.43 volts) for the thermionic work function at 1050°C. According to Suhrmann[9] the effect of electron bombardment on a specimen of gold is to displace the threshold from 2650–2700A to 2500–2550A, whereas a value of 2900A is reached after passing an electric discharge through hydrogen. Dubois[10] obtained an excursion of the phase boundary potential of 0.3 volt on admission of oxygen, whilst Whalley and Rideal[11] obtained an excursion of 1.56 volts on oxidation of a 'reduced' gold. Our first measurements with gold in air were made in the presence of mercury vapor and gave a sharp threshold at 2650±5A. Various treatments such as oxidation, reduction, adsorption of alcohol or iodine only effected a temporary alteration in this value to which it returned after removal of the adsorbed material. The presence of this threshold proved to be a sensitive test for mercury vapor and could be obtained at will. The same threshold was obtained with a silver white gold amalgam.

[5] Bosch, Ann. d. Physik **19**, 65 (1934).
[6] Morris, Phys. Rev. **37**, 1263 (1931).
[7] R. Suhrmann, Zeits. f. Physik **33**, 79 (1925); S. C. Roy, Proc. Roy. Soc. A**112**, 594 (1926).
[8] Goetz, Zeits. f. Physik **34**, 531 (1927).
[9] Suhrmann, Physik. Zeits. **30**, 939 (1929).
[10] Dubois, Ann. de physique **14**, 680 (1930).
[11] Whalley and Rideal, Proc. Roy. Soc. A**140**, 488 (1933).

In the complete absence of mercury vapor it was soon recognized that there were a few definite values to which the work function of gold after various treatments would spontaneously revert in course of time.

The threshold of gold washed after reduction with ethyl alcohol and left to stand in air was found to lie at 2520A (4.90 volts) and seemed to correspond to a stable oxide to which the gold surface eventually reverts in air even after drastic oxidation or reduction.

Oxidation by passing an electric discharge in air or oxygen imparts to the gold a characteristic threshold of 2360A (5.25 volts) whilst strong oxidation with nitric acid or heating to redness in air causes the formation of an almost photo-insensitive gold surface with a threshold at *ca.* $\lambda = 2150A$ (*ca.* 5.7 volts). By reduction in hydrogen the threshold shifted to longer wavelengths attaining a fairly stable value of 2950A. On re-admission of oxygen at room temperature the threshold slowly returns to the normal value of 2520A an indication of catalytic combination of the hydrogen on the surface. The greatest extension of the threshold in hydrogen was $\lambda = 3050A$ ($\phi = 4.02$ volts) obtained by continuous and vigorous reduction by discharge. The values obtained in this manner are compared in Table I.
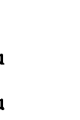
TABLE I.
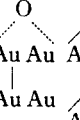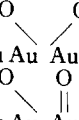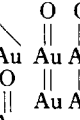
Author	Treatment	λ_0 Angstroms	ϕ Volts
Morris	Outgassing	~2100	
This work	Prolonged oxidation by nitric acid or heat	*ca.*2170	*ca.*5.6
" "	Oxidation by electric discharge in air	2360	5.25
" "	Normal value in air	2520	4.90
Morris	Outgassing	2560	4.83
Suhrmann	Reduction in hydrogen	2900	4.25
This work	" " "	2950	4.20
" "	Extreme value on reduction	3050	4.02
Morris	Extreme value on outgassing	3200	3.85

with those obtained by other methods. The maximum excursion obtained between the oxidized and reduced forms is *ca.* 1.58 volts comparable to 1.56 volts obtained by Rideal and Whalley and about 2.0 volts by Morris. It is evident that the values obtained with the quantum counter agree closely with those derived by the normal photoelectric or by the thermionic methods and further suggest that the

oxidation of reduced gold takes place in two well-defined steps with respective increases of 0.70 and 0.35 volt in the work function, of which the latter was obtained also by Dubois.[10]

It is interesting to note that these regular increments in the work function on progressive oxidation suggest that the work function of clean gold is 4.20 volts and that the increments are directly connected with the change in valency of the surface atoms of gold on oxidation. We obtain the following series:

Compound	$\begin{matrix} \text{Au Au} \\ \text{Au Au} \end{matrix}$	$\begin{matrix} \text{O} \\ \diagdown \\ \text{Au Au} \\ | \\ \text{Au Au} \end{matrix}$	$\begin{matrix} \text{O} \\ \diagup \diagdown \\ \text{Au Au} \\ \text{O} \quad \text{O} \\ \diagup \diagdown \\ \text{Au Au} \end{matrix}$	$\begin{matrix} \text{O} \\ \diagup \diagdown \\ \text{Au Au} \\ || \quad || \\ \text{Au Au} \end{matrix}$	$\begin{matrix} \text{O} \quad \text{O} \\ || \quad || \\ \text{Au Au} \\ || \quad || \\ \text{Au Au} \end{matrix}$
ϕ volts.	4.20	(4.55)	4.90	5.25	5.6
$\Delta\phi$ volts.		0.35	0.35	0.35	0.35

The excursion of 1.40 volts may be compared with the value of 1.365 volts obtained by A. Gerke and M. Rourke[12] for the potential of what was believed to be the gold auric oxide electrode at 25°C. No higher oxide was detected and the lower oxides were found to be unstable.

From experiments both on the accommodation coefficients of gases at metal surfaces examined by Roberts[13] and from the exhaustive work of Dubridge[14] and of Cassel and Glückauf[15] on the thermionic behavior of platinum it is shown that it is extremely difficult to obtain and maintain a clean surface of a metal for any period longer than a few minutes. The interior of a thin metal wire proves to be a copious source of gas which slowly diffuses out with a relatively high energy of activation. For platinum at least ten hours at 1370°K are required with a temperature coefficient of the order of 2.1 an almost endless period would be necessary at 900°K, the maximum temperature available for gold. A temporarily clean surface can be obtained by flashing or in the case of an oxide film by removal of this film by combustion with hydrogen.

[12] A. Gerke and M. Rourke, J. Am. Chem. Soc. 49, 1855 (1927).
[13] Roberts, Proc. Camb. Phil. Soc. 30, 74 (1934).
[14] Dubridge, Phys. Rev. 29, 451 (1927); 31, 236 (1928); 32, 961 (1928).
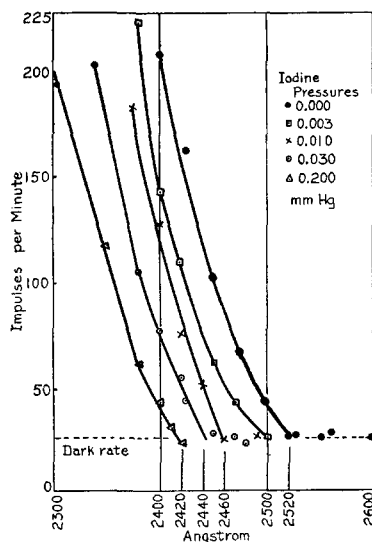[15] Cassel and Glückauf, Zeits. f. physik. Chemie 4, 347 (1932).

FIG. 3.

THE ADSORPTION OF IODINE ON GOLD

If iodine vapor be admitted to the gold surface in the presence of air, the threshold is displaced towards shorter wavelengths by an amount increasing with the iodine pressure up to a limiting value reached at saturation pressure. The process is readily reversible and in all cases the values of the thresholds could be reproduced within ±5A even after intervals of several weeks during which the gold had undergone various treatments. Some of the curves obtained are shown in Fig. 3.

Only at saturation pressure does the working of the counter become rather critical resulting in less definite results. If the gold be left in iodine at saturation pressure for some hours, much longer periods are required for desorption of the iodine, there is a marked decrease in photoelectric sensitivity suggesting a slow building up of a thick layer which is further confirmed by a gradual darkening of the color of the gold. During desorption gas could be admitted at regular intervals of time and the thresholds quickly estimated before continuing the desorption, a series of operations that could be performed in about three minutes.

Typical results for the process of removal of iodine from a slightly amalgamated gold surface are given in Table II.

TABLE II.

Time in minutes	Before adsorption	0	10	20	30	90
Threshold (A)	2650	2390	2450	2490	2520	2640

The results obtained at a series of iodine pressures are summarized in Table III and Fig. 4.

The curves obtained have the form of the Langmuir adsorption isotherms when $\Delta\phi$ is plotted against the iodine pressure, suggesting that the change in the work function is proportional to the amount of iodine adsorbed. This is probably due to the fact that since even at saturation the alteration in the work function of the gold surface by the adsorbed iodine is relatively small, the effective strength of the adsorbed dipoles must be small, thus no dispersive forces of any considerable magnitude come into play. In the last column of Table III are given the values of $\Delta\phi$ calculated according to the equation

$$\Delta\phi = \bar{\Delta}\phi_m \cdot ap/(1+ap).$$

There is a good agreement between the experimental and calculated figures. According to Campbell[16] at 25°C the dissociation pressure of aurous iodide is 95 percent of the saturation pressure of iodine vapor, thus in agreement with the present experimental data no thick film of surface iodide is formed except near the saturation point and no breaks in the $\Delta\phi$, p curves are
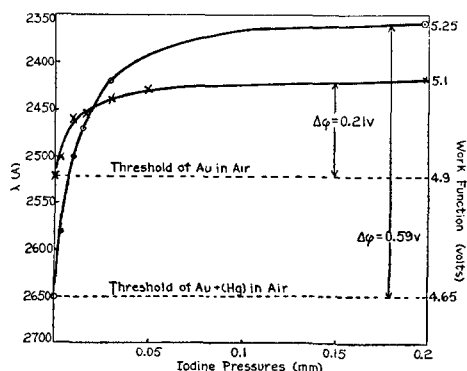

FIG. 4.

[16] F. Campbell, Chem. News 96, 15 (1907).

TABLE III.

TEMP. OF I_2 (°C)	VAPOR PRESSURE OF I_2 (mm Hg)	THRESHOLD (A)	φ (volts)	$\Delta\varphi$ obs.	$\Delta\varphi$ calc.
					$a = 162.5$
Absence of Hg vapor					$\Delta\phi_m = 0.21$
	0.000	2520	4.89	0.00	0.00
−20	0.003	2500	4.93	0.04	0.069
−10	0.010	2460	5.02	0.13	_0.13_
− 5	0.017	2455	5.03	0.14	0.15
0	0.030	2440	5.06	0.17	0.17
+ 5.4	0.05	2430	5.08	0.19	0.19
+20	0.2	2420	5.10	0.21	_0.21_
					$a = 84.5$
Presence of Hg vapor					$\Delta\phi_m = 0.59$
	0.000	2650	4.66	0.00	0.00
−20	0.003	2580	4.78	0.12	0.12
−10	0.010	2500	4.93	0.27	_0.27_
− 5	0.017	2470	5.00	0.34	0.35
0	0.03	2420	5.10	0.44	0.43
+18	0.17	2360	5.25	0.59	0.56

found as in the case of oxygen where one may presume the existence of a number of definite surface oxides. Similar phenomena were observed in the cases both of bromine on gold $\Delta\phi_m = 0.32$ volt and of iodine on silver and on a tungsten (WO) surface with respective thresholds of $\lambda_{Ag} = 2800A$ $\lambda_{WO} = 2810A$ and changes in the work function at saturation of $\Delta\phi_m \cdot Ag\text{-}I = 0.40$ volt and $\Delta\phi_m$ WO-I $= 0.20$ volt, respectively, but the relatively rapid formation of thick films with consequent loss of photoelectric sensitivity at these temperatures rendered the gold iodine system much more suitable for detailed investigation.

THE ADSORPTION OF ORGANIC VAPORS ON GOLD

It is well known that in the case of van der Waals' adsorption of organic vapors by charcoals and by metals the form of the adsorption isotherm is sigmoid and a number of interpretations have been given in explanation of this fact. There is strong evidence for the assumption that the low pressure portion corresponds to a Langmuir adsorption isotherm. On continued increase of pressure this is sometimes followed by a short or long period of pressure increase with but a relatively small increase in the amount of vapor adsorbed. This portion in turn precedes a further steady rise in adsorption with the pressure. Occasionally near the saturation point a marked rise is again noted. These phe-

nomena have been variously interpreted as due to the formation of multimolecular layers, or as due to condensation in microcapillaries. A third view suggests that it marks the transition from a two-dimension "vapor" obeying the Langmuir adsorption isotherm to a two-dimensional liquid phase resulting in the formation of islands of liquid monolayers at the expense of the vapor phase and that it is not until the liquid phase is complete and the pressure almost at saturation that flooding of the capillaries takes place.

It is evident if the third hypothesis be correct that over a more or less extended portion of the p, x curve the surface will be composite in character consisting of patches of two-dimensional vapor and liquid phases, the latter increasing as the pressure increases (isobaric growth will not occur until the liquid phases are large enough to be unaffected by the change in surface tension with the curvature). We might anticipate that the photoelectric thresholds of the surface covered with vapor and liquid phases, respectively, might differ from one another provided that the relative rate of electron emission was greater than the rate of compensation taking place across the composite film to re-establish a surface of uniform potential, and we should thus observe, at any rate with large islands, the phenomenon of a composite surface with two thresholds.

Double thresholds have been found in thermionic emission from sensitized potassium surfaces and also with tungsten.[17] The method of exploring the surface with the aid of a quantum counter is evidently more direct than that derived by the thermionic method as it gives immediate information about both the depth of the depressions in the surface energy barrier and the fraction of the surface they cover.

Preliminary experiments with various vapors in the counter revealed that petrol ether was without effect and that no change in threshold occurred with benzene at 3 mm and 30 mm Hg pressure, chloroform at 2, 5 or 17 mm and carbon tetrachloride at 10 and 25 mm although in all

[17] O. W. Richardson and K. T. Compton, Phil. Mag. 26, 549 (1913); O. W. Richardson and A. F. A. Young, Proc. Roy. Soc. A107, 377 (1925); A. F. A. Young, ibid. A104, 611 (1923); H. R. Laird, Phys. Rev. 34, 463 (1929); H. A. Warner, Phys. Rev. 37, 233 (1933).
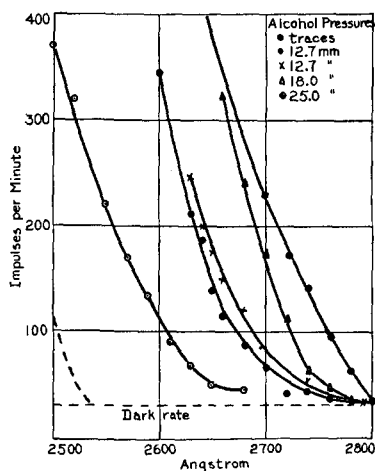
FIG. 5.

three cases the intensity of the emission decreased considerably with rise in pressure. Since these vapors possess absorption bands in this region, the possibilities of a surface action being involved are masked by the screening effect.

Carbon disulphide vapor in the presence of air exhibited an interesting behavior at a weakly amalgamated gold surface. The photoelectric threshold of 2650A was unaltered by the carbon disulphide, but upon irradiation with light within the region $2650 < \lambda < 2800A$ periodic bursts of activity were noted occurring at fairly regular intervals of about one minute. The gold surface in the counter eventually developed a reddish color. Light $\lambda > 2800A$ is without effect, the transition being fairly sharp. The phenomenon occasionally exhibited fatigue but the activity could be readily restored to the initial conditions by irradiating a few minutes with light of $\lambda < 2650A$. The photochemical action involved is probably a surface action since no ionization could be detected in the vapor phase by Hughes[18] in the full radiation of a mercury arc through a quartz window.

The counter works well in ethyl ether alone at a pressure of 60 mm Hg and also in acetone and ethyl alcohol in air. These substances on adsorp-

tion bring about a reduction in the work function, but the photoelectric behavior of the surface with variation in the partial pressure of the vapor is quite different from that exhibited by oxygen or the halogens. Starting with a low pressure of alcohol (Fig. 5) there appears at the foot of the curve a tail extending towards longer wavelengths. As the pressure is increased this tail gradually swells and its limit on the λ axis becomes more and more definite until this limit itself becomes the foot of a steeply rising emission at $\lambda = 2800A$ and can be considered as the threshold of the new surface. The phenomenon is completely reversible. It is remarkable that the value of the shift of threshold $\lambda = 2520A$ to $\lambda = 2800 = -0.49$ volt is obtained whether the original gold surface had a threshold value of $\lambda = 2650A$ due to traces of mercury or even when heavily amalgamated or whether, when mercury is absent, gold in its reduced or one of its oxidized forms is employed. Thus with gold with an oxidized surface with threshold at $\lambda = 2360A$ (5.25 volts) the shift was -0.49 volt and with gold with a surface in a more reduced state with threshold at $\lambda = 2520A$ (4.90 volts) (see p. 152) an identical shift of the threshold with the alcohol was obtained. If the alcohol vapor be left in contact with the gold for several hours, a slow reduction of the surface oxide layer occurs as revealed by a shift of its photoelectric threshold to somewhat longer wavelengths, which on standing gradually returned to the normal value obtained in air.

The presence of mercury vapor enhances and stabilizes the photoelectric emission in the region of the tail, although it does not alter the essential features of the phenomenon which appears on mercury free and on heavily amalgamated gold.

Acetone and ethyl ether also give a similar variation in thresholds; some of the curves obtained for the latter substance are shown in Fig. 6. The source was an iron arc.

The two thresholds for the original slightly amalgamated gold (2650A) and for the saturated surface (2800A) are clearly evident, but the definitely step-like character of the curves is partly attributable to the absorption of light by the vapor for both acetone and ethyl ether possess absorption bands in this region.

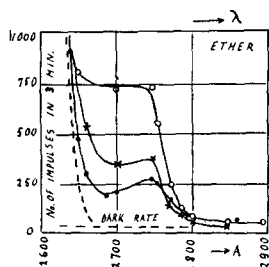[18] A. L. Hughes, Proc. Camb. Phil. Soc. 16, 375 (1911)

FIG. 6. Adsorption of ethyl ether on gold. Ether pressures: dots, 1 min.; circles, 5 min.; crosses, 15 min.

FIG. 7.

If an iron arc which possesses a number of strong emission lines in the neighborhood of $\lambda = 2800A$ be employed instead of the hydrogen lamp for the investigation of ethyl alcohol the step-like character of the emission as a function of the pressure displayed by ethyl ether is found in this case also. This permitted of an approximate valuation of the intensity of emission as a function of the alcohol pressure, and was found to be roughly proportional to the square root of the pressure.

It is clear that we are dealing with a case of double thresholds; one of the original surface practically unaffected and the other one -0.49 volt removed from it. It is only the intensity of the emission in the region between the two thresholds which increases with increasing pressure. It seems very likely since the effect is common to the three substances of which ethyl alcohol possesses no absorption bands in this region that the effect is located at the surface of the gold (Fig. 7).

The presence of a positive adsorbed layer would cause the initial surface potential barrier to change from form (a) to (b) and as L. Nordheim and R. H. Fowler[19] have shown the transmission coefficient through an ideal square shouldered hump is finite and equal to

$$\overline{D} = 8(\pi)^{\frac{1}{2}}[(kTC)^{\frac{1}{2}}/B]e^{-2xl(B-C)^{\frac{1}{2}}},$$

where B is the total height of the hump and C that of the barrier outside the hump. There is no emission at all for $W < C$. Thus for energies $W > B$ we have the ordinary emission of gold and
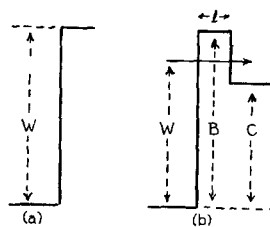
for $C < W < B$ we obtain the emission tail due to the adsorbed alcohol. If an increase in the alcohol concentration increases $(B - C)$, $\overline{D}$ will increase and the photosensitivity will rise in agreement with experiments. But the tail should also become longer, as C decreases with increasing alcohol concentration and this is not reconcilable with the experimental fact that the threshold of the tail is independent of the pressure of the alcohol. It is clear that leakage through the barrier plays an unimportant role in this case. The most satisfactory hypothesis is to consider the phenomenon as due to the formation of islands and the number or total area of these increasing with the pressure. We thus have two different types of emitting surfaces; that of the bare gold (or covered with vapor) with a full barrier of type (a) and height B and that of the gold covered with a two-dimensional liquid phase with a barrier of type (b) including a thin wall of height $B - C$, through which transmission takes place. As the pressure increases, $B - C$ remains constant, i.e., we still have the same two work functions, but the area of the islands increases until, when the whole surface is covered, the threshold of bare gold has entirely disappeared.

Finally we may note that while the threshold curves generally show an asymptotic approach to the wavelength axis, many of the curves are surprisingly sharp. Since only the electrons in the Sommerfeld levels of maximum energy are responsible for photoelectric emission,[20] sharp thresholds should be expected only at 0°K. As the field gradient on the tube cathode is not very high it seems unlikely that it could assist in pulling out all the electrons of the top level

[19] L. Nordheim and R. H. Fowler, Zeits. f. Physik **46**, 833 (1928); Proc. Roy. Soc. **A122**, 36 (1929).

[20] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

and so sharpen the threshold. Although the steepness of the curves can be accounted for by the magnification of the intensity axis due to the high sensitivity of the counter, the same would apply to the temperature tail and its absence is somewhat remarkable.

SUMMARY

(1) A photoelectric counter has been used for measuring quantitatively the changes in the work function of gold due to adsorbed layers. The high sensitivity of the counter permits an accurate determination of the threshold with monochromatic light from a continuous ultra-violet spectrum of moderate intensity.

(2) The work functions of strongly oxidized and strongly reduced gold differ by 1.58 volts. The oxidation proceeds over two definite steps, with respective increases of 0.35 volt and 0.70 volt in the work function.

(3) The adsorption of iodine vapor on gold at room temperature is reversible and the resulting increase $\sim\Delta$ in the work function varies continuously with the iodine pressure according to a Langmuir isotherm. The value of $\Delta\varphi$ at saturation is 0.2 volt.

(4) The adsorption of ethyl alcohol on gold gives rise to a double threshold consisting of (a) the original threshold of gold and (b) a new threshold corresponding to a decrease of 0.49 volt in the work function, this value being independent of the alcohol pressure. The intensity of the emission at the new threshold increases with increasing pressure. This suggests that the alcohol is condensed in the form of two-dimensional liquid islands, the area covered by these islands increasing with pressure.

The Liquid "Structure" of Methyl Alcohol

W. H. ZACHARIASEN, *Ryerson Physical Laboratory, University of Chicago*

Fourier integral analyses of the x-ray diffraction patterns of liquid nonyl and methyl alcohol are made. From these the radial distribution of atoms around any one atom is obtained. On the basis of the radial distribution curves, conclusions are drawn concerning the molecular configuration in the liquid. For nonyl alcohol this analysis confirms the results of Warren. In the case of methyl alcohol the analysis gives strong indication of hydrogen binding (dipole binding) between oxygen atoms of neighboring molecules. The short "life" of a given intermolecular bond in the liquid is emphasized. It is pointed out that the application of the ordinary Bragg equation to the peaks in the diffraction pattern of a liquid has no justification.

INTRODUCTION

RECENTLY B. E. Warren[1] published a paper dealing with x-ray diffraction in long chain liquids. He postulated a reasonable "structure" model of these liquids and showed that the diffraction curve calculated on the basis of the model was in agreement with the experimental curves measured by G. W. Stewart and collaborators. Warren considered the length of the chains to be practically unlimited, thereby neglecting the effect which the presence of the end groups of the molecules have on the scattering curve. (It should be mentioned, however, that he gives an interesting explanation of the so-called "inner" peak in the diffraction curve in terms of the length of the molecule.) This effect becomes increasingly important as the number of carbon atoms in the chain decreases. It is therefore not surprising that the diffraction curve calculated by Warren shows little resemblance to the experimental curve of say methyl alcohol.

[1] B. E. Warren, Phys. Rev. **44**, 969 (1933).