THE INFLUENCE OF OCCLUDED GASES ON THE PHOTO-ELECTRIC EFFECT.[1]

BY ROBERT JAMES PIERSOL.

THE part played by the gaseous films and occluded gases in the photo-electric effect has been studied by many investigators, who have not reached consistent conclusions.

Cantor[1] and Knoblauch[2] found that reducing agents and bodies not fully oxidized lose a negative charge rapidly when illuminated by ultra-violet light. Oxidizing agents and bodies which are oxidized do not lose a negative charge. Since a metal seems to give off more photo-electrons during oxidation, they concluded that the photo-electric effect is due to oxidation of the surface illuminated by ultra-violet light.

On the other hand, Chrisler[3] holds the view that hydrogen is essential to the photo-electric current, so that if it were possible to remove all occluded hydrogen there would be no photo-electric effect. Hydrogen has a very high coefficient of diffusion. Hence it is difficult to remove all occluded hydrogen from a metal. Palladium, in particular, has a high power of absorption for this gas.

Kustner[5] found that there seems to be no evident photo-electric effect in zinc after it had been scraped in vacuo. He took precautions to exclude all active gases from the metal.

Wiedemann and Hallwachs[6] supposedly removed the occluded gases from potassium by seven consecutive distillations, which seemed to cause the photo-electric effect to disappear entirely. Fredenhagen[7] confirmed these results in a similar series of experiments. Stumpf[8] obtained results by heating palladium electrically, from which he assumed a final zero effect. Paech[9] found that the photo-electric effect of a metal is dependent upon the gases which may be occluded such as oxygen, hydrogen, carbon dioxide, helium and argon.

[1] Accepted by the University of California in partial satisfaction of the requirements for the degree of doctor of philosophy.

[2] Wien. Sitzunger., 102, p. 1138, 1893.

[3] Zeit. f. phys. Chemie, 29, p. 527, 1899.

[4] PHYS. REV., 27, p. 267, 1908.

[5] Phys. Zeits., 2, p. 68, 1914.

[6] Verh. d. deut. phys. Ges., 2, p. 107, 1914.

[7] Verh. d. deut. phys. Ges., 5, p. 201, 1914.

[8] Verh. d. deut. phys. Ges., 22, p. 989, 1914.

[9] Ann. d. Phys., 43, p. 35, 1914.

On the contrary, Pohl and Pringsheim,[1] experimenting with potassium in vacuo, found that it behaved in practically the same way after repeated distillations. This would seem to show that there is an intrinsic photo-electric effect which is independent of occluded gases.

Hennings[2] studied the mutual relations of contact potential and the photo-electric properties of metals in vacuo, using a revolving knife edge to scrape new surfaces within the vacuum. His results show "(*a*) metals are more electro-positive when scraped in vacuo, but gradually become electro-negative with time; (*b*) photo-electric sensitiveness is increased by the removal of surface films; and (*c*) without films the photo-electric sensitiveness agrees exactly with the order of the Volta contact series."

Hughes,[3] in studying the contact difference of metals, has shown that initially there is but little contact difference of potential between distilled bismuth and zinc, as compared with platinum. A trace of admitted air greatly increased this difference. He showed that the change is located at the surface which becomes electro-positive.

Hartley[4] attempted to ascertain the electrical condition of a gold surface during the absorption of gases. The use of gold is favorable because it does not form chemical compounds easily. He showed that "(*a*) the gold surface acquires a negative charge during the catalytic combustion of gases in contact with it; (*b*) the electrical effect is antecedent to the actual combustion and primarily is due to the occlusion of gases; and (*c*) the metal becomes negatively charged during the removal of occluded hydrogen and positively charged during the removal of occluded oxygen."

Stoletow[5] found that the photo-electric effect increases in heating platinum to 200° C., but his results are complicated with secondary maxima and minima.

Zeleny[6] showed that the photo-electric effect of a heated platinum wire at first diminishes, reaching a minimum between 100° C. and 200° C., and subsequently increases to about 700° C., where its value is twice that at room temperature.

Varley and Unwin[7] confirmed these experiments, heating platinum foil.

Millikan and Winchester[8] studied the influence of temperature on photo-electric effects in high vacuum. Below 125° C., rise of tempera-

[1] Verh. d. deut. phys. Ges., 7, p. 336, 1914.
[2] PHYS. REV., 3, p. 228, 1914.
[3] Phil. Mag., 27, p. 170, 1913.
[4] Roy. Soc. Proc., 90, p. 9, 1914.
[5] Comptes Rendus, 108, p. 1241, 1889.
[6] PHYS. REV., 12, p. 321, 1901.
[7] Roy. Soc. Proc., 27, p. 117, 1907.
[8] Phil. Mag., 14, p. 188, 1907.

ture did not effect nickel, silver, gold, copper, iron, zinc, lead and aluminum.

Millikan[1] found that for sodium an equilibrium condition took place in the contact difference of potential about an hour after it had been cut in a vacuum of about 0.001 cm. of gas pressure. This constant potential was accompanied by constant and very large saturation currents. He assumed that this constant state was due to a state of equilibrium of the occluded gases.

Ladenburg[2] investigated platinum, gold and iridium in a very good vacuum at high temperatures. He found a maximum about 100° C. By heating and cooling several times in succession, this maximum effect disappears almost entirely. He attributes this to water vapor. Also he supposes that an increase near 800° C. is due to resonance.

The purpose of this investigation was to obtain definite data which will give additional light on the fundamental nature of the photo-electric effect. There was a desire to establish the relations of the saturation current with respect to occluded gases. We shall define the saturation current as the maximum value of the photo-electric current obtained by an electric field of sufficient gradient to sweep all the negative electrons to the receiving electrode. The data will increase the evidence as to whether the photo-electric effect is due to (*a*) an intrinsic property of the metal; (*b*) a surface film due to the oozing out of occluded gases; or (*c*) both an intrinsic property of the metal and a secondary effect due to gaseous films.

The apparatus, as shown in Fig. 1, consists of a heavy brass vacuum case *A*, put to earth. Coaxial with the case, a brass gauze cylinder *B* is supported by the rod *C*. The cylinder is copper-plated so that it may be blackened by oxidation. The metallic strip *D* is supported by the brass terminals *E*, which pass through a ground glass joint *F*. The terminals end in mercury cups, to which may be connected either the secondary of a transformer or any desired potential. In series with the primary of the transformer there is a choke-coil so calibrated that there is a scale which reads the amperes passing through the metallic strip. A circular quartz plate *G*, 0.1 cm. in thickness and 2 cm. in diameter, ground with its optical axis perpendicular to its surface, serves to transmit the ultra-violet light. The source of illumination is a mercury vapor lamp, focused on the metallic strip by a quartz lens. The receiving gauze cylinder is connected through a key *H* to a quadrant electrometer *I*, which has a sensibility of 50 divisions per volt on a scale at a distance of

[1] PHYS. REV., 3, p. 355, 1916.

[2] Verh. d. deut. phys. Ges., 9, p. 165, 1907.

one meter. The key is as shown, with a Victrola needle J, put to earth, which makes connection with a soft iron plate K, supported by a sulphur column, fixed to a solid iron base. The glass window L assists in focusing. The opening M leads to a Gaede rotary mercury pump, which gives a desired vacuum, less than 0.0002 cm. of mercury pressure, read by a McLeod gauge. The metallic strip is 1.5″ (3.809 cm.) in length, 0.5″ (1.270 cm.) in width, and 0.002″ (0.005 cm.) in thickness.

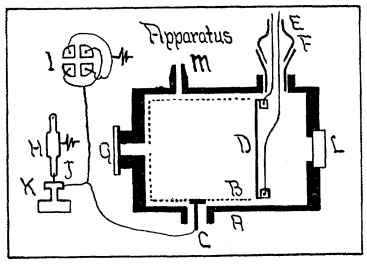

Fig. 1.

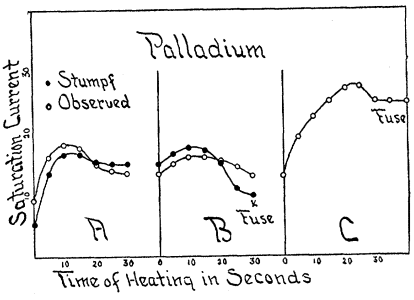

Fig. 2.

Preliminary experiments were made with palladium in order to verify Stumpf's results. He used the method of repeated heatings at increasing temperatures. By using arbitrary heating currents through the palladium, results were obtained as shown in Fig. 2. Divisions A, B and C of the figure represent successive increases of heating current. Each observation was taken after the occluded gases were pumped out for 5 minutes, the strip having been heated for 5 seconds. It may be noted that the sensibility of the final reading x, which Stumpf observed, was about twice the magnitude of the initial condition before heating. Yet he assumed that he would have reached a final zero value, due to the slope of the curve at x, with additional heatings, if the strip had not fused. It was possible to heat the strip at a higher temperature as shown in division C. Much difficulty was due to the sputtering effect, which decreased the thickness of the strip, therefore in order to heat the strip to the same temperature it was necessary to diminish slightly the heating current at each heating. The data for higher temperature would seem to indicate that the conclusions of Stumpf were not final.

There was a desire to establish the relation of the pressure of gas emitted to the photo-electric current. In Fig. 3 curve A and curve B This suggests that there may be a relation between the amount of gas driven off by heating and the saturation current. It is possible that the heavier occluded gases are driven off between 30 and 50 amperes, causing show the saturation current and pressure of emitted gas respectively as

plotted against heatings at increasing amperage. The saturation current was measured in divisions of deflection per second of the electrometer. Before each heating the pump was stopped and immediately after heating the increase of pressure was measured by a McLeod gauge. Then the gas was pumped out for 5 minutes, after which the saturation current was measured. A marked similarity exists between the two curves.

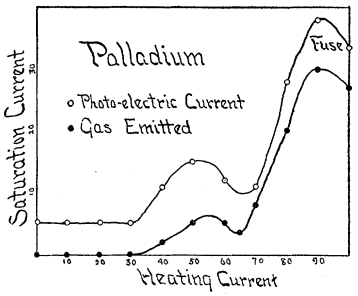

Fig. 3.

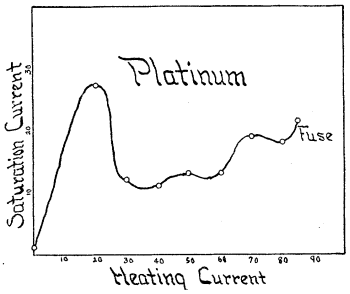

Fig. 4.

an increasing saturation current. Practically all these heavier gases escape below 65 amperes. This inactive condition of the occluded gases causes a decrease in current. Then the lighter gases begin to escape, and there are changes until all these gases are removed at about 90 amperes. Attempts were made to verify this point experimentally by spectrum analysis of the gases emitted at each temperature, but the work was brought to an end for the present, due to my departure from the university to pursue other work.

In the final results extreme care was taken to exclude from the system all stop-cock grease and water vapor. The metallic strips were handled with care so as to keep them free from any impurity. The sensibility of the electrometer remained constant (50 divisions per volt.) Between series of experiments it was necessary to re-focus the ultra-violet lamp, so that it may be necessary to multiply the magnitude of the saturation current by a constant due to a possible change in intensity of light, should it be desired to compare the values for two different metals. But the saturation currents for each series are absolutely comparable. The potential of the heating current is 10 volts, with a range from 0 to 250 amperes. All heatings were for a period of 10 seconds, the emitted gas being pumped out for 5 minutes before each observation was taken. A field of 100 volts was kept between the emitting and receiving electrodes to insure a saturation current.

The effect of heating platinum is shown in Fig. 4. The one striking characteristic is the large magnitude of the saturation current at 20

amperes. Fig. 5 shows the same series with a new piece of platinum with numerous readings near the sudden increase. This confirms the previous curve. Fig. 6 shows the effect of repeated heating of the same piece of

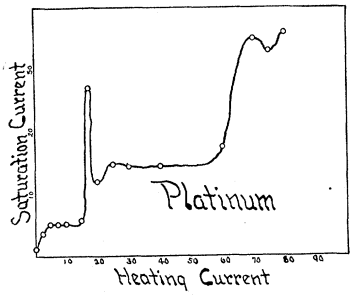

Fig. 5.

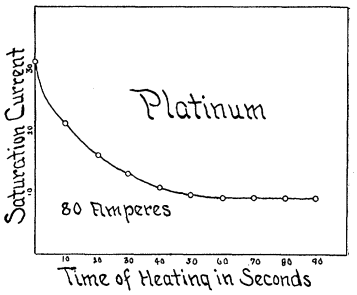

Fig. 6.

platinum immediately after the last experiment, without receiving the strip from vacuum. This gives evidence that the saturation current drops to a constant value with repeated heating to the temperature due to 80 amperes, which is very near the fusion point. In order to confirm this constant saturation current value, a new piece of platinum was heated at 80 amperes, 60 times in vacuo, to drive off all occluded gases possible. Then a series of observations were taken with increasin heatings from 0 to 80 amperes in order to ascertain if the sudden increase in the region of 20 amperes still existed. Fig. 7 shows that the condition which caused the sudden increase, together with the other irregularities, has been removed. This would seem to show that no more occluded gases were driven off at a temperature below the fusion point. The close agreement of the values for the saturation current is more apparent when tabulated as shown in the original form in the following table:

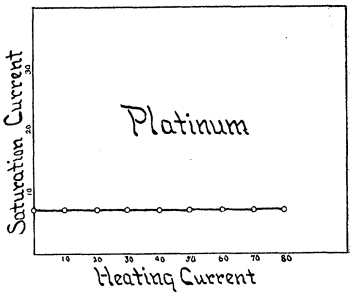

Fig. 7.

Amp.	Div.	Sec.	Div./Sec.
0	20	2.8	7.1
20	20	2.8	7.1
30	20	2.9	6.9
40	20	2.8	7.1
50	20	2.9	6.9
60	20	2.6	7.4
70	20	2.8	7.1
80	20	2.8	7.1

The effect of heating gold is shown in Fig. 8. Gold has a low point of fusion (60 amperes) which is the temperature region of initial maximum emission of gases. A new piece of gold was heated 35 times at 60 amperes, when it seemed to have come to a constant value. Fig. 9 shows that

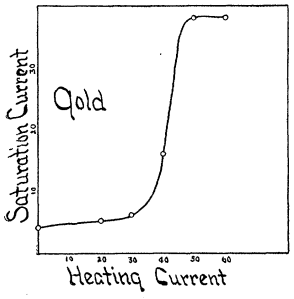

Fig. 8.

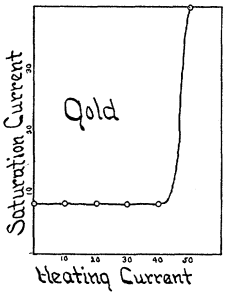

Fig. 9.

sufficient occluded gases still remain in the gold to give unstable conditions at the critical temperature of gas emission. In a continuous experiment the gold was heated 15 times at 50 amperes. The saturation current continued to increase.

The characteristic irregularities of nickel are shown in Fig. 10. Fig. 11 shows the results of a second series of readings with a new piece of nickel, observed in order to establish the maximum condition at 20

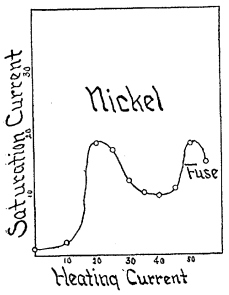

Fig. 10.

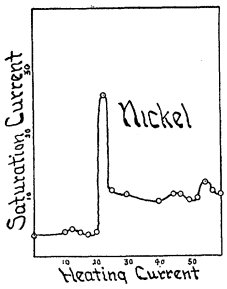

Fig. 11.

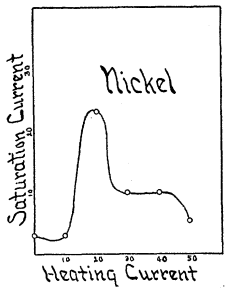

Fig. 12.

amperes. Fig. 12 shows the next series, with new nickel, which was obtained by driving off the occluded gases at each temperature until a constant value for that temperature was obtained. The heating was repeated 15 times at 20 amperes. The final constant values are shown. This seems to establish the conclusion that, below a critical temperature, repeated heating does not drive off all the gas, but some remains active at the surface of the metal. In a continuous experiment the same piece of nickel is heated 8 additional times at 50 amperes. Fig. 13 shows the results for heatings at increasing temperatures.

The effect of absorption was studied in order to determine whether the maximum saturation current is due to the emission rather than the absorption of gases. After the strip of nickel had been heated at the critical temperature due to 20 amperes, it was permitted to absorb gases under atmospheric conditions for given periods of time. Before each absorption the apparatus was evacuated in order to determine the saturation current. The following table shows the results.

Absorption	*Div./Sec.*
0 sec.	32.6
5 min.	29.2
10 min.	25.4
15 min.	25.0
22 hrs.	17.6
30 hrs.	12.4

After the final reading the nickel was heated at 20 amperes. The maximum effect increased to 6 times the maximum effect due to first heating. This might suggest that the nickel occluded more gases after the process of heating.

Fig. 14 shows the results of heating palladium. A new piece of palladium is heated 8 times near fusion when a constant value is reached.

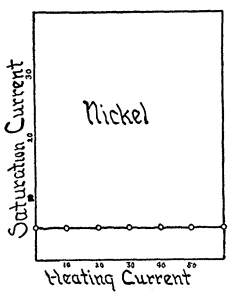

Fig. 13.

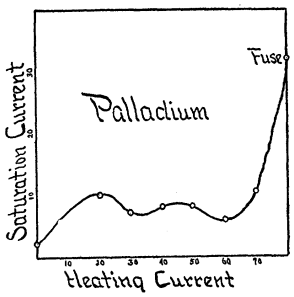

Fig. 14.

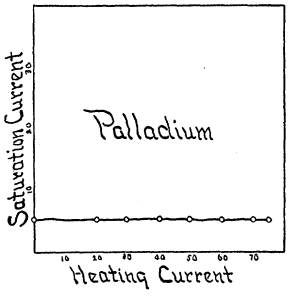

Fig. 15.

Fig. 15 shows that the saturation current is constant with respect to increasing temperature.

The influence of occluded gases on the photo-electric effect of silver is shown in Fig. 16. Although silver fuses at a lower temperature than gold, yet it was found to be possible to drive off the gases causing the maximum saturation current with 25 heatings. The results are shown in Fig. 17.

In a discussion of the results it is interesting to note that the method of heating metallic strips electrically in vacuo presents an easy and efficient method of cleaning the surface of the metal. This is true especially

in metals like palladium where the sputtering effect occurs at high temperatures. At each heating the surface is renewed. Also the high temperature tends to break down any existing gaseous surface film, the gas of which is pumped from the system.

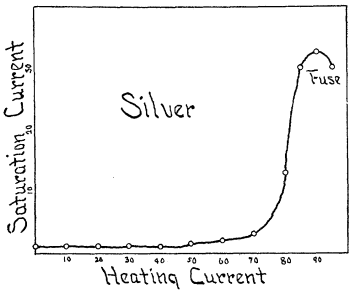

Fig. 16.

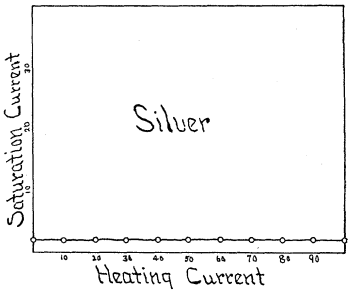

Fig. 17.

It is evident that the spurious effects are due to the gas driven to the surface rather than to the absorption of gas. At the critical temperature of maximum effect, the occluded gas is forced probably only to the surface, but is not ejected entirely. This is perhaps the reason why increased heating is necessary to remove the maximum effect.

These results give a valid proof for the assumption that the variation of the photo-electric effect with temperature is due to occluded gases. The maxima and minima of the photo-electric effect are due to occluded gases, corresponding to the maxima and minima of the photo-electric effect due to temperature as found by Ladenburg. This suggests that the effect of temperature on the saturation current is primarily an effect of the activity of the occluded gases at that temperature.

In this investigation of the influence of occluded gases the results are not confused by experimental conditions with the thermionic effects which are superposed on the photo-electric effect at high temperatures. This is because the observations were made after the metal was cooled to room temperature.

It does not seem probable that the maxima near 100° C. are due to water vapor as suggested by Ladenburg. The work was pursued at low pressures rather than under atmospheric conditions. Also there is no final increase at high temperature, necessitating explanation by a resonance theory.

The results due to the fact that gold fuses near the initial maximum, are of value in as much as they show that the occluded gases causing the abnormal increases in other metals have been removed. If the occluded gases were still present the critical effect would be permanent, as in gold.

Experimental data seem to give definite evidence in support of the following conclusions:

1. A photo-electric effect exists which is due entirely to an intrinsic property of the metal.

2. Superposed on this effect there is a maximum effect due to occluded gases.

3. The maximum effect is dependent upon the activity of the gaseous surface film (its magnitude being a function of the amount of gas driven to the surface).

4. The abnormal effects are due to the emission rather than the absorption of occluded gases.

5. In metals of high fusion point, a sufficient number of heatings drive off the occluded gases to such an extent that all abnormal effects disappear.

6. The photo-electric sensitiveness, after the emission of occluded gases, is larger than the effect noted before the expulsion of the gas.

Finally, it gives me pleasure to acknowledge the kindly suggestions of Professor E. P. Lewis, under whose direction the work has been pursued.

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