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ON THE VARIATIONS OF THE PHOTO-ELECTRIC CURRENT DUE TO HEATING AND THE OCCLUSION AND EMISSION OF GASES.

By L. A. Welo.

Introduction.

NEARLY all who have worked on the photo-electric effect have been aware of the strong influence of the surface conditions of the metal or of the effect of impurities which may be distributed throughout the body of the specimen under investigation. They have, however, concerned themselves only with the fullest possible elimination of these surface conditions or impurities by heating or scraping in high vacua; and, as far as the writer is aware, none have attempted to follow the course of the photo-sensitiveness at the various stages of cleaning until some measurements were made by Piersol[1] in this laboratory in 1916.

In addition to reporting on the changes in photo-sensitiveness of the cold metal after having been subjected to various degrees of heating in highly exhausted tubes, he shows that for palladium, at least, the amount of gas driven off is also large in intervals of high photo-sensitiveness and that the curve showing pressure change with heating current through the strip of metal closely parallels the heating current-photo current curve. The intimation is plain that different gases come off at different heating currents, and that the photo-electric current is affected by their kind.

It was this possibility that gave rise to the present investigation. Its immediate object was to examine, spectroscopically, the gases emitted by metals at different degrees of heating and to make the corresponding measurements of the photo-electric current after the metal had been allowed to cool to room temperature.

The Apparatus and the Experimental Procedure.

The simple apparatus shown in Fig. 1 consists really of two parts; the photo-electric cell proper and the Plücker tube for the examination

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[1] Phys. Rev., 8, 238, 1916.

of the gases. An essential feature is the total small free space (about 4 c.c.) attained by using tubing only slightly larger than the mounting shown hatched in the figure. This mounting is a piece of porcelain tubing pierced by two heavy copper leads. The leads have pieces of spring brass attached at the lower ends, pressing against the tongue formed by grinding away a part of the porcelain. The thin strips of metal of dimensions 6 × 38 mm. are bent to form a U and the ends slipped under the brass pieces. When thus mounted, the total radiation from the quartz mercury arc entering from the right and passing the cylindrical anode does not strike the middle of the strip. That the part subjected to radiation is of sensibly the same temperature as the middle is proven in that the strips fused above the corners of the U quite as often as between them. The ground joint at the top makes renewal of the metal strips easy. The parts of the apparatus that cannot be fused are joined with De Khotinsky cement.

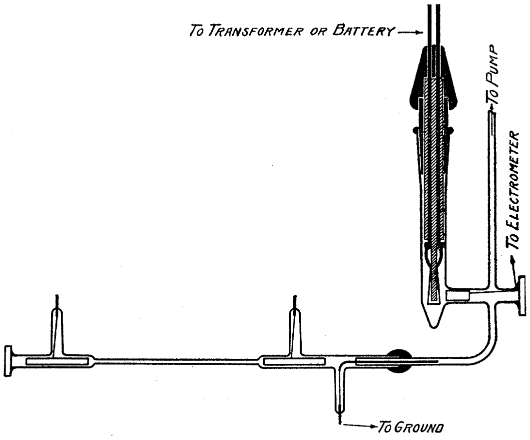

Fig. 1.

Spectroscopic observations were made with both a small quartz spectrograph and a direct-vision instrument. The electrode marked "to ground" was in contact with some fine wires nearly filling the capillary joining the parts of the apparatus. The idea was that they might shield the cell from the discharge taking place while spectrograms were being taken. A deteriorating influence on the photo-electric behavior was sometimes noted unless this precaution was taken. The photo-currents, which were all within the range 1.6×10^{-12} and 1.0×10^{-10} amperes, were measured by the rate-of-charging method with a Dolezalek electrometer of sensibility of 50 divisions per volt. All of them are saturation values insured by joining one of the copper leads to the negative pole at a 100-volt battery, the other pole being earthed. When the strip was to be heated the battery connection was broken and the copper leads attached to a stepdown transformer with choke coil control. A transformer also produced the discharge in the Plücker tube.

A Gaede mercury rotary pump produced vacua so high that the discharge failed to pass through the Plücker tube with a 12 cm. spark gap in parallel, after the strip had been heated to high temperatures. Before so treated, gases are continually being emitted at ordinary temperatures and pressures less than 0.002 mm., gauge measure, cannot be obtained. During a part of the time mercury vapor was kept out with liquid air or absorbing alloys. Its presence is, apparently, without influence on the photo-electric effect. Except when gas was actually being driven off and tested the cell was always in communication with P_2O_5. In common with others who have done spectroscopic work with vacuum tubes at very low pressures, it was found impossible to get entirely rid of the lines and bands of traces of carbon compounds, cyanogen and water vapor. That such high vacua can be obtained after thorough heating of the strips shows that these traces come largely from the strip itself and not from the glass or De Khotinsky cement nor from the stopcock grease. At any rate there is no danger of confusing these traces of impurities with the very copious supplies of gas emitted by the metals at certain heating currents.

The usual experimental procedure is as follows: The pump connection is closed and the heating current sent through for eight periods of 25 seconds each. The spectrograms are then taken and notes made during the while of what is seen in the direct vision instrument. The gas is pumped out and by this time the metal has cooled nearly to room temperature, permitting two measurements of the photo-electric current. The metal is again heated with pump going and on cooling two new measurements are made. Following the second heating of four 25-second periods the photo-current is usually in agreement with that after the first to within 5 per cent. If it is not, there is alternate heating and measurements, after cooling, until two successive currents agree satisfactorily. At low heating currents the eight 25-second periods can as well be combined into one or two such that the total time of heating is 200 seconds. If enough gas is obtained on two or three heatings it may be examined and the pump run during the remainder of the 200 seconds of heating.

THE RESULTS.

The results of the photo-electric measurements are concisely presented in the curves. The last heating current is that at which the metal fused so that the entire range of available temperatures is covered. The brackets above the curves summarize the changes in the gases emitted. "None" indicates that under the brackets so labelled there was either no gas emitted or there was not enough to permit the discharge to pass. The brackets labelled "hydrogen" need no explanation. Those marked "carbon" cover four possibilities. The carbon spectrum is given by CO_2, CO, some of the hydrocarbons and, as is well known, also by tubes filled with oxygen if carbon is present in some form; unless the supply is continually replaced by a fresh one, displacing the oxide formed with the carbon impurities on the glass, electrodes, etc., under the influence of the discharge. To the extent, then, that these four gases are liable to give the same spectrum the identity of the gas or gases coming off in the region marked "carbon" is an open question. Obviously, the usefulness of the spectroscope for such studies as these is at an end. Chemical analyses of these minute quantities of gas should be possible by the methods of Ramsay, Mond and Shield[1] or those lately used by Langmuir.[2] The changes from one gas to another are, of course, gradual and not so abrupt and definite as the brackets indicate. The brackets are placed after a thorough study of the spectrograms and after comparison with the notes made while observing visually.

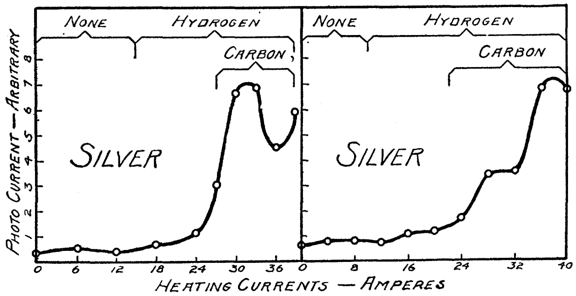

Fig. 2.

Fig. 2 shows what was obtained with two different pieces of silver The results of Piersol are verified; as the differences are not greater than those found among individual specimens. This metal shows a continual increase of photo-sensitiveness with increase of temperature (photo-currents measured after cooling) until a maximum is reached close to the fusion point. Beyond this a second maximum may begin to develop, as in the first sample, but usually the behavior is that of the second, where the metal fused while sensitiveness was on the decline. Hydrogen

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[1] Phil. Trans. Roy. Soc., 186, 657, 1895.

[2] Amer. Chem. Soc. Jl., 34, 1310, 1912.

comes off at all heatings beyond the interval labelled "none" and for a time it is the only gas. When photo-sensitiveness begins to climb, carbon compounds or oxygen come off the sensitive metal and their spectra are the most prominent at heating currents giving also maximum photo-sensitiveness. Like hydrogen, the carbon gases continue to come until the metal is fused.

The next curve is for one of four pieces of gold. Two of the others were like that shown. The third differed in that after reaching a maximum, the photo-effect remained constant and unaffected by further heating. The results are the same as for silver except that the emission of the gases giving the carbon spectrum ceases and at the two last heatings only hydrogen is evolved.

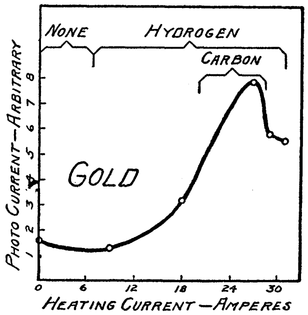


Fig. 3.

The spectra of the gases obtained from gold appear at the top of Plate 1. The numbers at the right indicate the heating current used for driving off the gas giving the spectrum. The spectrograms are those for capacity in the discharge circuit. The lines may be identified on reference to the legend at the foot of the plate. It is noted that all of the carbon lines are strong with the gas driven off at 27 Å., which current also gives the maximum photo-electric effect. The hydrogen lines H_α and H_β are out of the range of the spectrograph and with the small amounts of gas driven off from gold the less intense lines H_γ and H_δ could not be made to show on the photographs. Nearly all of what is being reported as to hydrogen is based on visual observations.

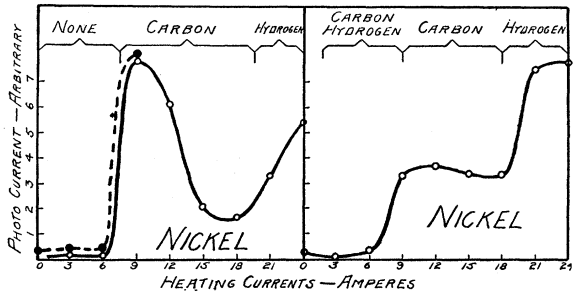


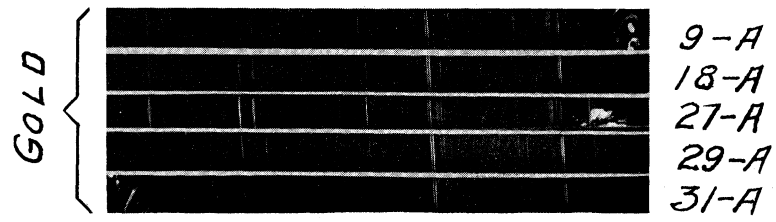
Fig. 4.

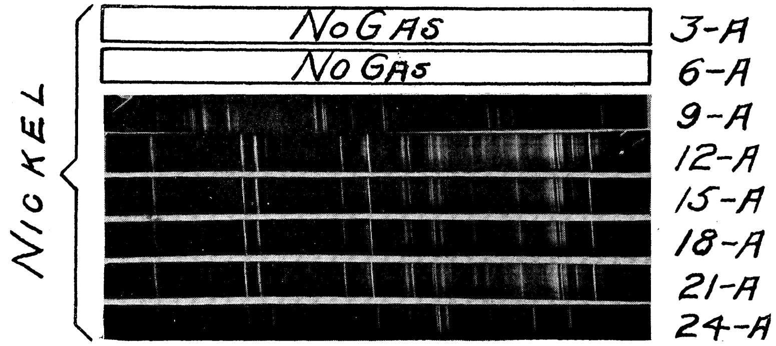
Three sets of data for nickel are presented in Fig. 4. The two curves which are complete illustrate the differences, with respect to both photo-sensitiveness and gas emission, that may be observed with different specimens of the same metal. On the other hand, if two strips are cut from the same sheet of metal, the effects are reproducible as indicated by the dotted and solid curves at the left. The measured ordinates for the dotted curve were multiplied by the factor 0.61 to secure this fit. The curve was not completed because the cell sprung a leak while heating at 12 amperes. At first sight, the completed curves appear vastly different. Still the only difference seems to be that the depression present in the first at 15 and 18 amperes was not allowed to develop in the second, and that photo-sensitiveness remained unusually constant for four different heatings. They both show fairly constant sensitiveness at the beginning and a steep climb on approaching fusion.

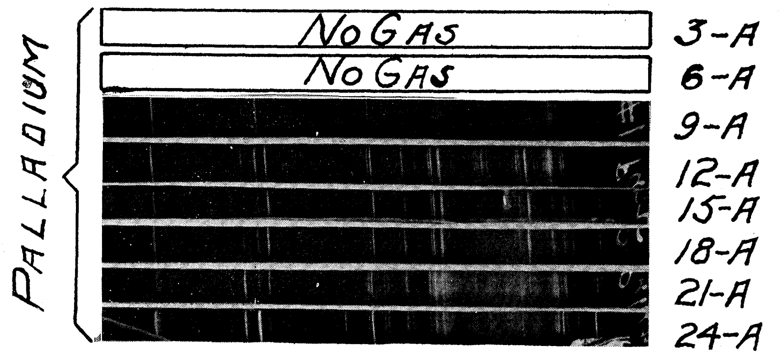
The indications for the gases in the panel to the left refer to the curve shown solid. Like silver and gold, nickel also emits carbon gases or oxygen at the temperature which gives the first maximum in the heating current-photo current curve. Unlike silver and gold, the gases are not mixed with hydrogen but come off alone. Self-induction in the discharge circuit affords a delicate test for hydrogen in a mixture of gases. The test gave no hydrogen in the visible for the gases driven off with 9 and 12 amperes. Traces began to appear at 15 and 18 amperes, and at the fusing current of 24 amperes hydrogen alone was found. The differences noted at lower heating currents are due to the use of a smaller cell while taking the second set of data. In the first specimen the cell was too large to give good gas pressures with small heating currents. The gases are denoted as "none" because they could not be examined.

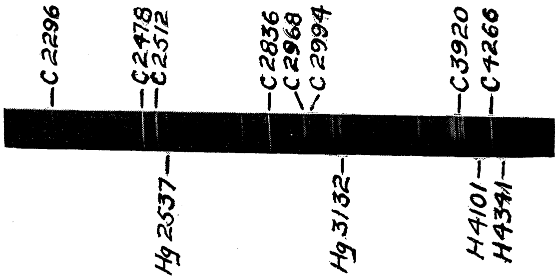
It is not exactly at the maximum of photo-sensitiveness that the carbon gases are alone or predominate but slightly beyond. The second curve shows this in that the first large value of the photo-current falls within the interval giving hydrogen and carbon. It is more forcibly brought out in the spectrograms which are to be taken in connection with the left-hand panel. At 9 amperes there are carbon lines, but they are more prominent at 12 amperes, in a region of descending photo-sensitiveness, and then become less and less intense relative to hydrogen. The last spectrogram shows a few faint carbon lines unavoidable in vacuum tube spectroscopy.

An interesting change in the appearance of the nickel may be noted. As it is obtained from the importers it is not shiny nor of a metallic luster as the other metals but looks like blue steel. The piece which was removed after heating at 12 amperes was white and had fully regained its luster. The large rise in the curves for nickel at 9 amperes is thus due to the removal of the visible deposit. Beyond 9 amperes for nickel, and


GOLD
9-A
18-A
27-A
29-A
31-A


NICKEL
No GAS
No GAS
3-A
6-A
9-A
12-A
15-A
18-A
21-A
24-A


PALLADIUM
No GAS
No GAS
3-A
6-A
9-A
12-A
15-A
18-A
21-A
24-A


C 2296
C 2478
C 2512
C 2836
C 2968
C 2994
C 3920
C 4266
Hg 2537
Hg 3132
H 4101
H 4341

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always with the other metals, the photo-electric changes are not accompanied by any visible changes of the surfaces.

The results for palladium, Fig. 5, are novel in that there are two narrow intervals in which carbon gases alone are emitted. Even self-induction in the circuit discloses no hydrogen. The carbon is not entirely absent in the interval marked "hydrogen" but the spectrograms for 15 and 18 amperes show carbon veryfaintly and in the visible region none at all is seen. At points just inside of the two maxima carbon is shown to be present in considerable quantities by the spectrograms for 12 and 21 amperes; but when one has a better basis for comparison, as in the visible where the hydrogen lines are strong, one sees that hydrogen is the principal gas where it is so indicated.

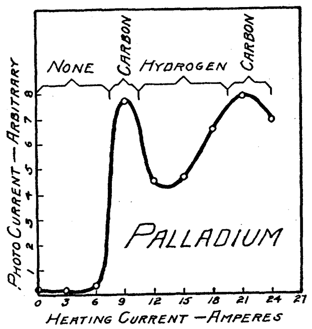

Fig. 5.

In the main, the two curves for the platinum of Fig. 6 agree. Only one principal maximum appears and at about the same heating current. The results for the gas analyses are identical. The spectrograms for this metal are not included. The very narrow peaks obtained by Piersol at 20 amperes on his scale of heating currents, and which should appear at about six here, were either missed or do not exist for this specimen.

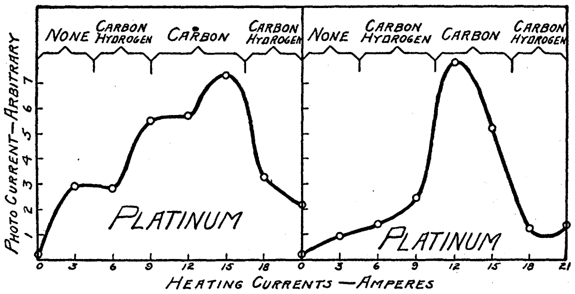

Fig. 6.

It is an interesting fact that if the point at the peak in Fig. 5 of his paper is disregarded, that curve will also show the two shelves on the ascending side. The gas analyses seem less definite with platinum than with the other metals. Hydrogen is never wholly absent, for in the intervals marked carbon the hydrogen spectrum is brought out with self-induction in the discharge circuit.

THE EFFECTS OF THE ADDED GASES.

On the completion of the tests which have been reported on in the preceding pages, it was thought that the work might most profitably be continued by treating the metals, cleaned by heating close to fusion in vacuum, with pure gases. The underlying idea was that it might be possible to imitate the original curves and identify more definitely the gases coming off as carbon compounds or oxygen. For this reason, most of the gases tried were hydrogen and those apt to give the carbon spectrum. Cyanogen was included because its bands are prominent among the impurities of the spectra. Nitrogen was expected to be without influence. The treatments accorded the metals were to let them stand, after cleaning, in the gas over night and sometimes even two weeks; or, to heat them in the gas close to fusion and gradually lower the temperature so a region of selective absorption should be passed through if one exists. A possible departure from the plan is to remove the metal from the cell, after heating, and charge it, electrolytically, with either hydrogen or oxygen or both. The photo-electric behavior of the metals after heating in plain or colored flames was also looked into with interesting results. The complete list of gases and conditions of treatment is contained in the columns at the left of Figs. 7 and 8. All of the gases, including air, were dried at least 24 hours over P_2O_5. As to their preparation and purification it is only necessary to say that Erdmann[1] was followed, except for nitrogen and hydrogen. Nitrogen was prepared by keeping air over a strong alkaline solution of pyrogallic acid. A similar solution also absorbed the oxygen gathered by diffusion by electrolytic hydrogen. No attempts were made to control the pressures while the gases surrounded the metals. The pressures were always high and anywhere from atmospheric to 30 cm. of mercury. Although the times of treatment with gas are indicated the use of them is made only in the discussion of results for palladium and platinum.

The scale of heating currents for each metal is given at the foot of each figure. Attention is called to the fact that each panel shows more than the variation of the photo-electric current with heat treatment. The constant photo-sensitiveness, obtained on sufficient heating at the cleaning temperature, is shown by the dot or ring through which the short arrow passes. The arrow is directed towards the point which measures photo-sensitiveness after treatment but before heating. Its slope is a rough measure of the rise, fall or constancy of photo-sensitiveness while the metal is being "gassed."

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[1] Lehrbuch der Anorganischen Chemie.

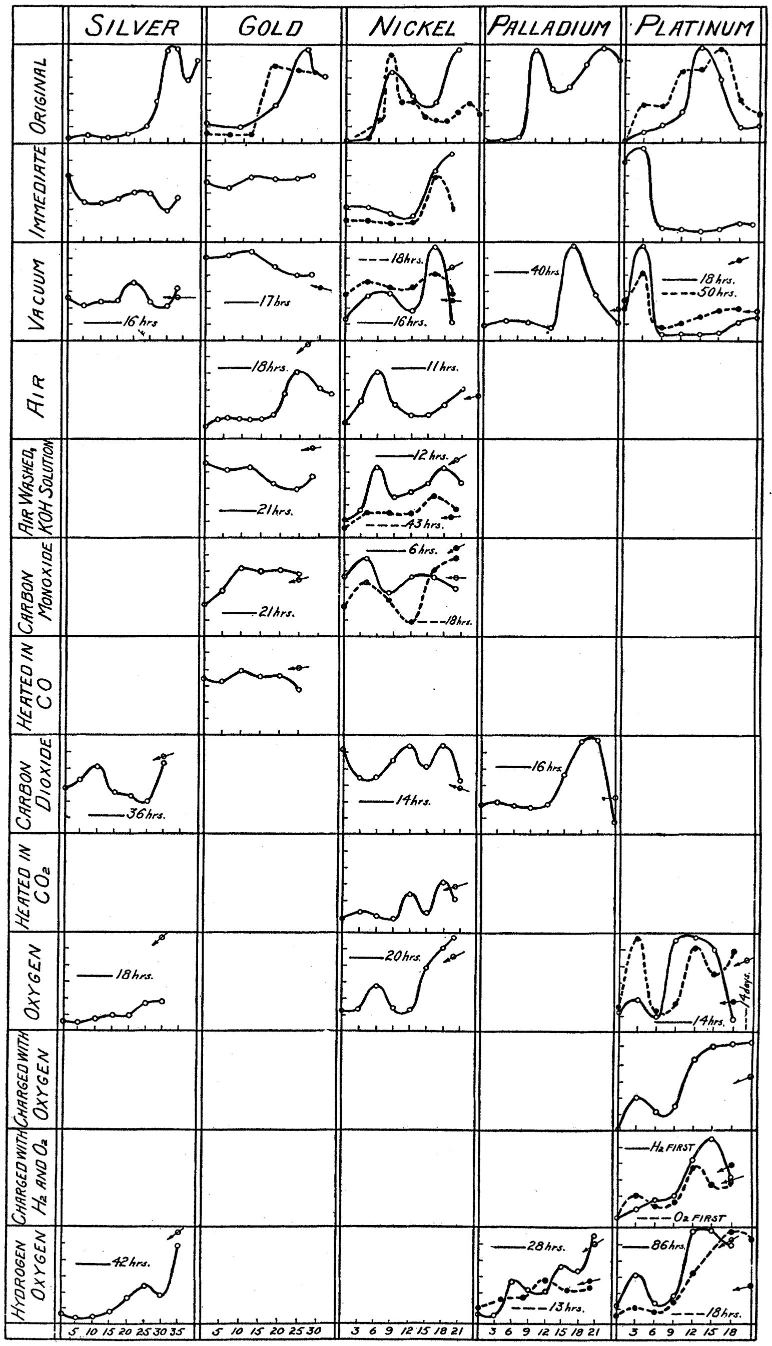
SILVER
GOLD
NICKEL
PALLADIUM
PLATINUM
ORIGINAL
IMMEDIATE
VACUUM
AIR
AIR WASHED, KOH SOLUTION
CARBON MONOXIDE
HEATED IN CO
CARBON DIOXIDE
HEATED IN CO_2
OXYGEN
CHARGED WITH OXYGEN
CHARGED WITH H_2 AND O_2
HYDROGEN OXYGEN
16 hrs
17 hrs
18 hrs.
16 hrs.
40 hrs.
18 hrs.
50 hrs.
18 hrs.
11 hrs.
21 hrs.
12 hrs.
43 hrs.
21 hrs.
6 hrs.
18 hrs.
36 hrs.
14 hrs.
16 hrs.
18 hrs.
20 hrs.
14 hrs.
14 days.
H_2 FIRST
O_2 FIRST
42 hrs.
28 hrs.
13 hrs.
86 hrs.
18 hrs.
5 10 15 20 25 30 35
5 10 15 20 25 30
3 6 9 12 15 18 21
3 6 9 12 15 18 21
3 6 9 12 15 18

Fig. 7.

All of the curves shown in solid lines in the row labelled "original" at the top of Fig. 7 will be recognized as some of those appearing in Figs. 2 to 6. Of the curves in the column for silver, those taken after treatment with hydrogen, oxygen or a mixture of the two, are the most illuminating. They illustrate one unusually good case of imitation of the original with the right combination of gases and how each produces its own independent effects.

It is seen that hydrogen does not lower the effect but raises it (arrow points upward slightly) and that the photo-effect is markedly constant until at the last heating current it is suddenly doubled. Oxygen, on the other hand, caused a drop from 104.5 to 10.6, and on heat treatment this sensitiveness is slowly trebled. In the mixture, the hydrogen has been able to bring about the sudden large increase on approaching the last heating current. At that point the oxygen which had the depressing and predominating influence on the sensitiveness is suddenly driven off as the spectroscopic data for the originals of Fig. 2 indicate, and the photo-current rises. If the oxygen were not so overpowering when it is present in silver the sensitiveness would certainly be higher in the interval of lower heating currents and would probably resemble the effects with hydrogen as to constancy also. If the comparison of the curve for mixed gases is made with the second curve of Fig. 2 it will be seen that both have a shelf or "kink" in the interval 28–32 amperes. It is not to be expected that the imitation should show the turn at the final heating because it is not at fusion, as is the original.

According to the information contained in the panel for carbon dioxide, this gas lowers the photo-electric effect but is far from being as disastrous as oxygen. Krüger and Taege[1] have examined the changes taking place when metals are surrounded by gas for short periods and report that with CO_2 the change is slight. The fall observed here is not slight. The truth seems to be that its influence is slight only when it is not the only gas present, as is not the case here.

It is further to be noted that the maximum at 10 amperes bears no relation to anything that is observed on the original, or the curve obtained after treatment with other gases. Carbon dioxide introduces features into cleaned nickel, also, which are observed nowhere else. As will presently be shown, it is without influence on even clean palladium. The view of the action of carbon dioxide which seems to be most consistent with what has been observed here and with published data is that it is without influence in the presence of other gases, such as oxygen and carbon monoxide. However, when these gases, including carbon dioxide,

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[1] Zeit. Elekt. Chem., 21, 562, 1915.

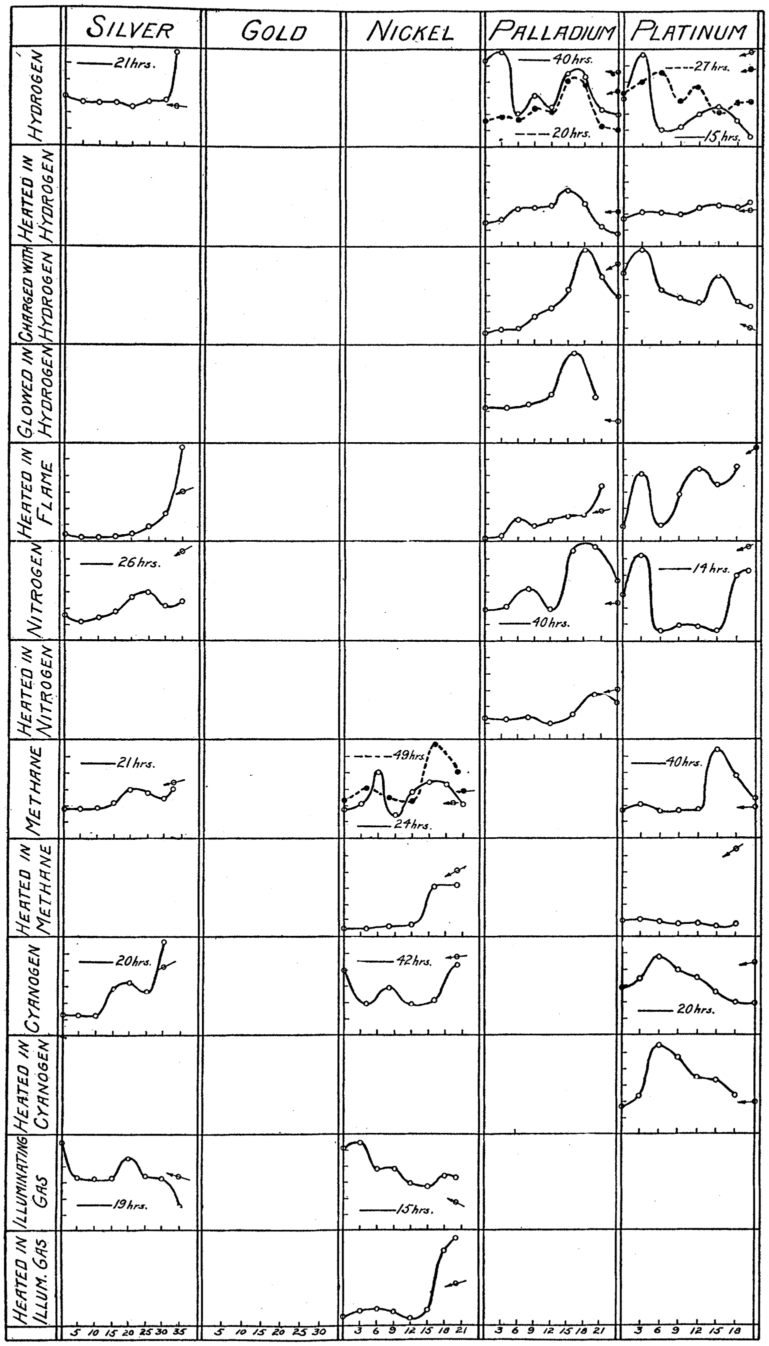
SILVER
GOLD
NICKEL
PALLADIUM
PLATINUM
HYDROGEN
HEATED IN HYDROGEN
CHARGED WITH HYDROGEN
GLOWED IN HYDROGEN
HEATED IN FLAME
NITROGEN
HEATED IN NITROGEN
METHANE
HEATED IN METHANE
CYANOGEN
HEATED IN CYANOGEN
ILLUMINATING GAS
HEATED IN ILLUM. GAS
21 hrs.
40 hrs.
20 hrs.
27 hrs.
15 hrs.
26 hrs.
40 hrs.
14 hrs.
21 hrs.
49 hrs.
24 hrs.
40 hrs.
20 hrs.
42 hrs.
20 hrs.
19 hrs.
15 hrs.
5 10 15 20 25 30 35
5 10 15 20 25 30
3 6 9 12 15 18 21
3 6 9 12 15 18 21
3 6 9 12 15 18

Fig. 8.

are removed by high heat in a vacuum and the carbon dioxide reintroduced a decreased photo-effect is observed with characteristic elevations and depressions in the heating current-photo current curves, of which there were no traces during the original cleaning.

When we are to make a decision as to the effects of the gases methane, cyanogen and nitrogen we need another basis of comparison than the original, for there is no similarity. This basis is gotten by going through a curve for a strip which has remained in a vacuum for several hours after cleaning; or better, one which has been gone through immediately. Such a curve is known as "immediate." The ordinate at zero amperes is really the ordinate which measures photo-sensitiveness after the strip has cooled from heating as close to fusion as possible. It is quite surprising that the variations should be so large and it is only with gold that anything like the expected constancy appears.

Let us turn for a moment from a discussion of the curves for silver and consider the effects of the gases experimented with on gold. It was thought at first that the curve for air gave the imitation of the original and that the active component was the carbon dioxide; for the curve is entirely different from that in the panel beneath. It has been shown, however, that CO_2 is inactive. The curve then does not illustrate the effect of the gas. It is included in the figure because it shows the existence of a lag between the emission of gas and the corresponding heating current and it shows also what happens when the cleaning is incomplete. What is to be noticed is that the gold was cleaned at 27 amperes and was fused after treatment at 33 amperes. In the vicinity of 27 amperes the curve is, after treatment, exactly like the original. The photo-current was not constant up to 27 amperes, as one would expect. The curve shows that the original cleaning at 27 amperes did not completely remove the gas which begins to come off then; although heating at 27 amperes was continued until constant photo-sensitiveness was attained. While most of a gas which begins to come off at a certain heating current is removed at that heating current it takes a higher temperature to remove the rest of the gas. A certain persistence shows itself. This view is in accord with what was seen in the Figs. 2 to 6. The heating currents at which gases showing carbon spectra first come off were quite definite but the same gases continued to come for two or three higher heating currents.

The immediate curve with gold shows an unusual constancy as compared with corresponding curves for the other metals. The depression at 6 amperes shows a slight fatigue. It should be remarked that it takes about 3 hours to obtain the data for a curve and that, with metals of such high electrical and heat conductivities as silver and gold, over an hour may elapse before one is far enough along to give temperatures sufficiently high to counteract the fatigue, whatever its cause may be. With the other metals, the temperatures are high even at the first heating current and they glow at 6 amperes. The reason that gold does not show the large variations in the immediate curve is connected with its chemical inactivity as compared with silver and nickel and that it does not possess the property to any extent of absorbing gases.

The remaining curves for gold show the characteristic "corner" at 12 amperes beyond which the photo-effect falls. The oxygen of the air and the carbon monoxide affect gold similarly. The changes found in gold in vacuum are due to traces of either or both of these gases in the cell. Examination of these curves in connection with corresponding curves for nickel makes it appear highly probable that it is the carbon monoxide. The oxygen acting on nickel gives an excellent imitation of the original shown solid, which is the most frequent type. It shows the narrow maximum around 6 or 9 amperes.

The carbon monoxide, however, gives for both of the curves of the panel the broad maximum extending from 0 to 12 amperes, which is clear and definite for the solid curve for vacuum and which shows itself also in the dotted. It is well to call attention here to the irregularities at the ends of all the nickel curves. They are either ascending or descending as the metal fuses. The reason is that the second maximum for the original nickel curves appears so close to the fusion point. The maximum is narrow and never located at exactly the same place; so it may happen that one specimen will fuse before the peak is reached, while another fuses after the high photo-sensitiveness is passed. This, together with the lag and the persistence of the gases noted for gold, makes it impossible to attach any importance to the latter parts of the nickel curves. That the behavior at the ends for nickel is quite independent of the gases used in treatment is further shown, in that the ends with all gases are the same as the ends of one or the other of the originals. This may even be said of the curve for illuminating gas. Comparison of the nickel curves for oxygen and air seems to indicate that oxygen gives a narrow maximum at six amperes and not a broad one such as comes with carbon monoxide and vacuum. In the lower dotted curve for air a different set of points was taken, so that the elevation was probably missed. Provisionally, until we have examined the effects of methane, we can say that it is the residual carbon monoxide which gives rise to the irregularities derived in the vacuum.

Returning now to the discussion of silver we notice that the vacuum, nitrogen, methane and cyanogen give curves of the same type. The photo-sensitiveness is constant until heating currents of 15 to 20 amperes are reached. Around 20 amperes there is an elevation followed by the normal rise on approaching fusion. The three gases mentioned have thus no effect on silver and are not even able to protect the specimen from the action of the residual gas. This gas is, provisionally, carbon monoxide; unless we are not dealing with the effects of a gas at all, but with some inherent impurity of the metal. This possibility will be considered in connection with the work on platinum.

The curve obtained with illuminating gas is an interesting one. The sharp maximum at 20 amperes is to be expected with any gas containing carbon monoxide. The rise in sensitiveness is unusual and is even more pronounced with nickel. The curve for the latter metal is very complex. The initial high value in both metals is due to some other gas than methane. Evidently it is easily driven from the silver, for beginning at 3 amperes, the photo-electric effect is constant until the elevation given by carbon monoxide is reached. Beyond this, there is constancy and then a sudden dip. One explanation of the fall is the presence of hydrogen sulphide. It was found by Krüger and Taege[1] that this and other catalytic poisons all lowered the photo-electric effect. It is necessary to assume, however, that the gas is driven off only with great difficulty and that the traces are active only when other gases have been removed. Small quantities may have been left on the walls of the cell. It could not have been on the silver, for the gas would have dissociated long before higher heating currents were used.

After silver, cleaned by heating in a vacuum, is further heated about a dozen times in a Bunsen flame, small irregularities are removed. Since cooling takes place in the oxygen of the air we find the small photo-sensitiveness at lower heating currents. If we had only the curves for silver to go by we should conclude that to imitate the originals it is only necessary to heat them as they were heated during the rolling; which, as the refiners state in a private letter, is with an air blast. Similar treatment of palladium and platinum fails to produce an imitation of any of the originals.

Although cyanogen and methane were not active on the silver the former affects the first reading on nickel and the latter gives curves of the same type as those for carbon monoxide. Although one of the methane curves shows a narrow maximum at 6 amperes the other is of the characteristic breadth. It becomes necessary to change our statement, made previously, that the effects introduced in the vacuum are due to carbon monoxide. It may be this gas or methane. In either

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[1] Loc. cit.

case the statement holds that cyanogen and nitrogen are without influence on silver.

One must not think that the first maximum in the original of nickel is related to methane, although the gas gives good imitation. The spectrum of methane shows hydrogen largely, whereas the gas emitted while the original curve is being run through shows no hydrogen, even when the attempt is made to bring out its lines with self-induction in the circuit. This observation practically eliminates the possibility that a hydrocarbon is one of the gases driven off in the intervals marked "carbon" in Figs. 2 to 6. The carbon dioxide has already been shown to be without effect when other gases are present, so that there are left to be included under the "carbon" spectrum only oxygen and carbon monoxide. With silver it is certainly oxygen. With gold and nickel no decision can be made.

Another observation is not out of the way here. On one occasion the cell and Plücker tube were joined by a capillary bent in the form of a U. The pressure was decreased on the immersion of the capillary in liquid air but the spectrum was unchanged in character. Mixtures of gases are thus seen to come off at times.

The cyanogen has only affected the first part of the curve for nickel. After standing 42 hours, the nickel has been slightly reduced in sensitiveness. This condition is easily removed, for at the first heating current the photo-sensitiveness is reduced to one half. The sharp maximum at 9 amperes and the appearance of the end of the curve indicates the presence of oxygen. A trace of oxygen would also account for the fact that with silver in cyanogen the three first ordinates are lower than is silver in methane, nitrogen and vacuum.

The curve for nickel in illuminating gas is altogether too complex to follow, but the same cause which increases the sensitiveness of silver acts on nickel also. One thing worth noticing about the two curves for illuminating gas is this: the latter part of the silver curve fits the curve for nickel from 3 to 12 amperes. It is to be remembered that larger currents are necessary to produce a given temperature with silver and gold than with the other metals. It appears that if we were using temperatures instead of heating currents as abscissæ we should obtain with illuminating gas, and very often other gases, similar curves for the different metals.

Usually, when metals are heated in any gas there is a sharp decrease in photo-sensitiveness. Heating nickel in methane conforms to the rule, and the usual constancy with increase of the temperature is also noted. The unusual feature is the sudden rise at 15 amperes. As it appears with methane it is to be expected with illuminating gas. The fall at the end of the curve for silver and noticeable also in nickel in illuminating gas does not appear after heating in the gas. The H_2S which probably caused it is decomposed as soon as the metal is heated above 310°.

We know from Fig. 4 that a gas giving the hydrogen spectrum comes from nickel at high heating currents. Methane and other hydrocarbons give this spectrum. There is a relation between this and the fact that after heating in methane and illuminating gas the high maxima, also appearing at the ends of the originals, are seen. Heating platinum in methane, on the other hand, gives a very constant photo-sensitiveness at all heating currents. A chemical analysis of the gases emitted on heating nickel would in all probability reveal, not only hydrogen in the intervals so labelled, but one or more hydrocarbons.

It is among the curves for palladium that we notice for the first time any influence of the time of standing in the gas. We see it in the palladium treated with hydrogen, oxygen and a mixture of the two. After palladium has been in the mixture for 13 hours it has developed a trace of irregularity and when the metal has stood for twice this time, two prominent maxima have appeared. They are nearly at the heating currents required for the imitation of the original curve for palladium. One reason why they are displaced to the left is that this specimen fused at 20 amperes instead of at 24 for the original. The effect of time is, however, even more noticeable with palladium in hydrogen. After standing for 20 hours, only, the last of the three maxima is fully developed. After 40 hours, two additional elevations barely traced before are fully developed and one of them to a very great extent. The maxima appearing in palladium at 15–18 amperes can be introduced into the curves by the hydrogen under all conditions of treatment and also by residual gases and vapors of the vacuum. It is more reasonable to think that carbon dioxide did not introduce the maxima but that this gas and the nitrogen failed to protect the palladium from the action of the residual gases. Perhaps hydrogen, too, is unable to give this protection. It seems that oxygen is essential in order to protect the metal from this action, for the maximum does not appear after heating in a flame: this process involving exposure to the oxygen of the air. The solid curve for hydrogen-oxygen indicates that even in the presence of oxygen, the elevation due to residual gases will develop if sufficient time is allowed.

Heating in hydrogen gives a different result from heating in any of the other gases; as there is a slight increase during heating instead of a very large fall in photo-sensitiveness. It is seen that on heating in hydrogen and nitrogen the shape of the curves obtained on merely standing in the gas is preserved. Platinum when so heated shows afterwards only small variations. By heating platinum in hydrogen or methane more constant photo-currents can be obtained than in any other way. Charging palladium electrolytically, and making it the cathode in a glow discharge results in identical heating current-photocurrent curves. A fall in sensitiveness is given during the first operation. The mere doubling of photo-sensitiveness seems small in the face of the results obtained in glowing the alkali metals, and those observed by Greinacher[1] on glowing with lead, zinc and platinum; but this is an isolated observation, whereas Greinacher's ratios (for platinum) vary from 1 to 100. The important thing here is that palladium thus treated gives the usual type of curve with hydrogen. The large drop when charging with hydrogen is due to the exposure to air during transfer to the electrolytic cell. Confinement in an atmosphere of hydrogen for 15 minutes before the transfer was tried as a means of preventing this action.

There is some good ground for the belief that nitrogen does affect palladium. There is also an elevation for palladium at 6 amperes on heating in the flame, involving contact with nitrogen during cooling. The sudden rise at the end of the platinum curve for this gas is surprising since the larger part of the curve is exactly like the immediate and vacuum curves for the same metal.

The high sensitiveness at 3 amperes and the unusual fall on going to 6 amperes is characteristic of nearly all the observations on platinum. The phenomenon can best be accounted for by the action of residual gases, since this feature is so marked in the curves for the vacuum. The appearance of the maximum in the immediate curve shows that the action is very rapid. The effect is undoubtedly connected with the observation made by Zeleny,[2] and subsequently by Davidson,[3] who studied the photo-effect of wires heated in air. A sudden dip took place in the temperature-photocurrent curves on passing through 100°. Zeleny believed the phenomenon due to properties of the metal itself but Davidson showed that it was due to occluded gases. It is well known that oxygen condenses on the surface of platinum, but the property does not depend on the temperature to any extent as compared with the property of palladium absorbing hydrogen at 100°. The curves already discussed have not indicated the presence of oxygen as a residual active gas and it is further seen that platinum must stand a long time in oxygen before

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[1] Deutsch. Phys. Gesell. Ber., 15, 797, 1913.

[2] Phys. Rev., 12, 321, 1901.

[3] Phys. Rev., 26, 1, 1908.

the high photo-sensitiveness at 3 amperes shows itself. In fact, oxygen seems, with cyanogen, to be the only gas capable of suppressing the high sensibility. The other gases, such as hydrogen and nitrogen, fail to protect the metal. When oxygen is present it takes a long time for the residual gas to bring about its effects. For instance, when platinum had been in oxygen 14 hours, the peak at 3 amperes is not pronounced while after similar treatment of another specimen for 14 days the peak is 3 times as high. A growth in the same ratio occurs when treated for different times in a mixture of hydrogen and oxygen.

The pronounced sensitiveness at 3 amperes cannot be accounted for on the theory of Richardson[1] that there are impurities in the platinum, mainly sodium and potassium, which are driven to the surface on heating, or even evaporated. Sheard and Woodbury,[2] while confirming Richardson's views in the field of positive ionization from hot metals, use as a part of their argument, the time variation of the thermionic current at 725° just after heating to 800°. Here, however, no decay was noticeable. The photo-measurements made after the two heatings at 3 amperes, cooling and evacuations were in agreement within the experimental error. There is a further difficulty with the view that we are dealing with some easily vaporized metallic impurity in the platinum. No such maximum at 3 amperes, with fall on going to six, is noticeable in the original curves. The peaks observed by Piersol are farther along on the curves (at 6 amperes on the present scale of heating currents). The absence of the effect from the originals is easily accounted for on the theory of the action of residual gases. They are unable to attack the platinum as long as it is protected by the gases already on the new strips. A remark in Davidson's paper is of significance here. He tells of having raised the platinum to a bright red heat before going through the curve with the dip at 100 degrees, similar to that seen here in passing from 3 to 6 amperes of heating current.

In all of the curves involving the presence of oxygen alone, or as a part of a mixture, the maxima of the original curves at 12 or 15 amperes appear: wholly in accord with the belief that all of the maxima may be attributed to oxygen—unless it be carbon monoxide. The two curves for hydrogen are inconsistent. The solid one, however, is not of different type from that gotten by charging with hydrogen electrolytically. As with palladium, it is shown that the manner of treating with a given gas is indifferent. Heating in a gas is another matter.

Charging platinum electrolytically with oxygen destroys its activity

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[1] Phil. Mag., 20, 545 and 981, 1910.

[2] PHYS. REV., 2, 288, 1913.

towards ultra-violet light. On heating, the activity is regained and follows the usual course for oxygen except at the end, where a high constant sensitivity is approached. It is worth mentioning that large quantities of gas were emitted at all heating currents beginning with 12 amperes, where photo-sensitiveness also is high for the first time. The curves in the panel marked "charged with H_2 and O_2" were taken after charging with both gases but in inverse orders. The time integrals of the charging currents are the same. The two curves bring out the fact that oxygen is the gas of predominating influence, even when the metal is so thoroughly treated with another gas as in the process of charging, electrolytically, with hydrogen.

The methane curve is interesting on account of the constancy until 15 amperes is reached. The effects of the residual gas have not been completely repressed because a small elevation shows itself at 3 amperes. The latter part of the curve is like the curve for hydrogen. The maxima at 15 amperes with platinum in hydrogen and methane are coincident with the maxima of the originals. As has been pointed out, there is a trace of hydrogen in the intervals of the original platinum curves marked "carbon" under proper conditions of the discharge. It is probable that with platinum, the maxima produced by more than one gas do coincide. Finally, leaving the curve for heating in flame to the next section, there remains only a consideration of the effects of cyanogen. The curves are of an entirely new kind. They are exceptional also in this: that heating in the gas gives the same type of curve as mere contact with gas and also does not lower the sensitiveness. The arrow has practically a zero slope.

The Effects of Heating in Flames.

Two considerations guided the work recorded in Fig. 9. One was the possibility of collecting easily ionizable active material from flames, plain or colored, and the other was that during manufacture the platinum was known to have been heated in the flames in lime crucibles. All five curves were taken with the same strip so that individual differences among specimens of platinum are eliminated. The flames raised the metal to a white heat. The heat was also white when the platinum was imbedded in pulverized lime.

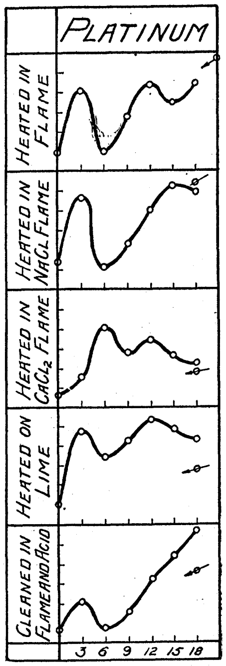

Fig. 9.

As to the type, the upper two curves do not differ from curves obtained after treatment with oxygen. During treatment in an uncolored flame the sensitiveness fell in the ratio 6.25 while with heating in the sodium chloride flame this ratio was 3.9. The salt thus leaves an activity. It is easily removed and has no influence on the curve that follows, for in both curves the sensitiveness, in going from 3 to 6 amperes, falls in the ratio 4.1. The effect of the residual gas causing the high sensitiveness at 3 amperes is visible.

Heating in a flame colored with calcium chloride does give immunity against residual gas Heating on lime does not. A still more photo-active material is left by the calcium than by the sodium salt for the drop in sensitiveness is only 2.7 (for both lime treatments) instead of the 3.9 for sodium and 6.25 for the uncolored flame. It is at the higher heating currents that the effect of calcium shows itself best. From 12 amperes on, the two are alike and also similar to the original curves for platinum, although the decrease in photo-sensitiveness is not so rapid. It has occurred to the writer that calcium carbonate may be the cause of the variations observed in the original curves and that the carbon spectrum is given by the carbon dioxide released on the dissociation of the carbonate. No data have been found as to the photo-electric properties of the calcium oxide which would thus be left on the platinum but Debye[1] and Richardson[2] have shown, theoretically, that an intimate relation exists between electron emission at high temperature and by ultra-violet light. In view of the use of lime for the Wehnelt cathode its photo-electric activity might be high. It is well to keep in mind that the behavior after heating on lime is not due to something remaining from the heating in calcium chloride flame. The platinum was used in the meantime for three of the curves of Fig. 7, namely, hydrogen for 15 hours, and the two for the metal charged electrolytically with both hydrogen and oxygen.

Concordant results could not be obtained by Davidson[3] in his study of ionization phenomena, by mere heating in a flame. Cleaning was accomplished by alternate dipping in acid and heating in flame while the metal was charged to a high negative potential if the impurity to be removed was alkaline earth. This plan was followed here and the last curve of Fig. 9 resulted. There was no immunity to residual vapors, as the maximum at 3 amperes shows. The platinum has been entirely freed of those irregularities, characteristic after treatment in calcium

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[1] Ann. d. Phys., 33, 441, 1910.

[2] Phil. Mag., 23, 263 and 594, 1912; 24, 570, 1912.

[3] Loc. cit.

or all of the gases. The only curve at all like it is that obtained on charging with oxygen electrolytically.

Some General Considerations and Suggestions for Further Experiments.

The experiments, the description of which forms the basis of this paper, are inadequate and our knowledge of the mechanism of occlusion and adsorption too meager to justify any theory of the variations at this stage. In this, the concluding section, then, a few of the possibilities will be considered and the means indicated of deciding among some of them.

A quite satisfactory theory of adsorption is that devised by Langmuir[1] and supported by his extensive studies of the electron emission and chemical reactions at low pressures and high temperatures, principally with tungsten and platinum. Taking the special case of oxygen adsorbed on tungsten: one single layer of oxygen atoms is joined to the surface layer of tungsten atoms because the two primary valences of oxygen are turned down and are saturated by the tungsten atoms. In the case of carbon monoxide, two of the four primary carbon valences are turned down and saturated by the tungsten so that the diagrammatic representation will consist of the surface layer of tungsten atoms, then a layer of carbon atoms, and finally, on top, a layer of oxygen atoms whose two primary valences are saturated by the two carbon valences turned upward. The nitrogen atoms are mutually very thoroughly saturated, so that this gas is held to a surface only by weak secondary forces and thus is not readily adsorbed. The important thing, in connection with the present subject, is that only one layer can be formed. The forces holding the possible second or third layers would be weak so that the number of atoms in these layers would be negligible. The extent of adsorption is, thus, determined by the area of metal covered with atoms of gas.

The elimination of the adsorbed layer by heating or other means is, then, to be looked upon as the formation of gaps in the surface layer and further cleaning merely as an increase in the areas of the patches of bare metal. Assuming that only the bare metal is photo-sensitive, the rise in the photo-electric current is also accounted for. The fall of the photo-current beyond the maximum can be explained by the formation, at particular temperatures and pressures, of a new layer of another gas. No observation has been made on platinum, but one for tungsten is reported on by Langmuir.[2] In speaking of the impossibility of dis-

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[1] Amer. Chem. Soc. Jl., 38, 2221, 1916, and Phys. Rev., 8, 149, 1916.

[2] Amer. Chem. Soc. Jl., 38, 2272, 1916.

sociating hydrogen with an oxygen-covered filament or of causing chemical combination of the two gases, even at a temperature of 1200°, he says: "If, however, we assume that the oxygen atoms are chemically combined to the mass of the tungsten filament and forms a *continuous* surface layer, all of the observed facts are readily accounted for. The oxygen atoms are saturated chemically by the tungsten (primary valence) and the field of force holding the oxygen atoms lies wholly below the surface where the hydrogen molecules cannot reach it. When the pressure of oxygen falls so low that the supply of this gas at the surface is not sufficient to make up for the loss by evaporation, the gaps are formed in the continuous covering and the hydrogen is then able to make a *flank attack* on the oxygen. In this way the oxygen covering is *suddenly* removed when the pressure of oxygen falls below a certain critical value, and the dissociation of hydrogen, therefore, begins at once." The sudden removal of oxygen is significant in the light of the spectroscopic results in our original curves. Here is a case of the removal of one adsorbed layer facilitating the access and formation of a new one from residual vapors or gases. This layer causes a depression in the heating current-photo current curve until clean patches of metal begin to appear at higher temperatures. The removal of this second layer might facilitate the formation of a third layer bringing about the descent from the second maximum in the curve for palladium, Fig. 5. It would seem that a study of the photo-electric current from tungsten along the lines of the present paper might be undertaken with profit. In view of the extended experimental work of the last 6 years by Langmuir it is almost certain that more is known of the behavior of tungsten towards gases than of any other one metal.

The older, or transition layer, theory of adsorption can account very well for the photo-electric phenomena, if it is taken in connection with the notion of solution of a gas in a solid and with some recent observations of Cardani.[1] We must look upon the layer as merely hindering the escape of electrons released from the metals. The gradual reduction in thickness or density of the layer will permit more and more of them to escape. To account for a depression in the curve, after the original layer has been broken up, a new layer must be formed. The gas for this must come from within the metal and, according to Cardani's results with the aluminum electrodes in X-ray tubes, this is quite possible. "The occluded gas" he found, quoting the abstract, "experiences very great difficulty in reaching the surface of the electrodes, even under the influence of high temperature and rarefaction, and the electrodes may

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[1] Accad. Lincei, Atti, 24, 105, 1915.

consequently undergo superficial exhaustion and the pressure remain constant during the passage of the discharge for some days, so long indeed as the occluded gas in the deeper layers fails to compensate the exhaustion when it reaches the surface; when, however, such compensation does occur emission of gas recommences on the discharge being passed." In the experiments with which we are here concerned, the compensation is initiated by the heating at higher temperatures and there may be a great deal more than mere compensation. In fact, enough gas yielded by the metal to build up a new layer capable of remaining for several heatings. This way of looking at the phenomena is quite consistent with the observed fact that the readily diffused hydrogen appears in all but very narrow intervals of the curves. It is a matter of indifference on this view whether the gas on the surface originally and that which finally diffuses out is the same or different in kind.

In the above it has been assumed that the photo-sensitiveness is a property of the metal itself and that the gases only modify the conditions of escape of the electrons. But the changes in photo-sensitiveness can also be accounted for on the basis of the changes of the properties of the metals themselves, either by solution in it of gas or by the formation of chemical compounds. These changes need take place only at the surface but may extend throughout the metal. Heating merely changes the concentration of gas or dissociates or builds up different compounds. The last seems more probable for the changes would be expected to take place at certain temperatures, giving rise to definitely placed elevations and depressions in the curves. The first is not entirely excluded, as the function relating photo-sensitiveness to concentration of gas is not necessarily a continuously increasing or decreasing one.

No evidence is at hand bearing on the question of concentration of gas but good ground exists for believing that chemical changes play an important part. Millikan and Souder[1] working with sodium and Wertheimer[2] with cadmium have found differently shaped fatigue curves according to the wave-lengths in use. The only explanation seems to be that active gases, even undetected traces, form chemical compounds which respond to different spectral regions than the metals themselves. Of course in the original curves these active gases are of no consequence. Once the metal has been cleaned the gases can, however, assert themselves.

The two above mentioned papers have suggested a test that it is hoped to carry out soon. If, instead of the total radiation, two extreme

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[1] Proc. Nat. Acad. Sci., 2, 19, 1916.

[2] Deutsch, Phys. Gesell. Ber. 17, 289, 1915.

ends of the spectral region for which the metal is sensitive, are used and differently shaped heating current-photo current curves result, it is proof that chemical changes take place, or a change of concentration, which alters the long wave limit of sensitiveness or the activity for a given wave-length. If the curves for the two monochromatic radiations are similar we should have to reject the idea of change of concentration of gas or of chemical change and attribute the variations of photo-sensitiveness to the opening up of gaps through the one atom layer or a reduction in its thickness or density. Of course no decision can be reached, by this means, between the two theories of adsorption.

The comparison of curves for different wave-lengths should reveal the presence of metallic impurities on the surfaces of the metals being investigated. If, as has been suggested, sodium and potassium are driven from the body of, say, platinum to its surface, it might, at certain temperatures, show the photo-electric effect well into the visible region of the spectrum.

A test of the two adsorption theories would be afforded by working in vacua of a far higher order than have been available hitherto. An extreme vacuum would prevent the formation of the second or succeeding layers of atoms of gas and the photo-sensitiveness remain constant once the clean patches of metal have grown to cover the entire surface. Heating current-photo current curves should have the appearance of the saturation curves for currents in ionized gases. In the transition layer theory, on the other hand, where the gases all come from the metal; the state of the vacuum is relatively unimportant, if it only is high enough to prevent ionization currents.

Still another mechanism, not to be lightly thrown aside is suggested by an examination of the curves of Robinson[1] and Stuhlmann and Compton[2] relating the photo-electric current to the thickness of sputtered platinum films. Robinson's curves are particularly similar to our original curves for nickel and two of the curves shown by the latter authors are exactly like the present curve for platinum charged electrolytically with oxygen and for platinum cleaned in flame and acid, as far as they go. In general, such exact similarity is not to be expected because of the complication of many gases and the presence of metallic impurities. With platinum charged with oxygen, the other gases are well subdued and heating the metal in flame and acid is an effective means of getting rid of salts and metallic impurities. It may be imagined that the cleaning by heating is a sort of an ingrowing surface phenomenon. Each heating

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[1] Phil. Mag., 32, 421, 1916.

[2] PHYS. REV., 2, 199, 1913.

removes completely a certain thickness of gas, leaving a thin sheet of pure metal. On increased heating the sheet gets thicker, passing that of maximum photo-sensitiveness. At this time the gas in the body of the metal may diffuse all at once to the surface, as in Cardani's[1] experiments, and contaminate the cleaned layer. The process of cleaning is then repeated at higher temperatures and a second maximum of the heating current-photo current curve gone through. It might also be assumed that the photo-electric activity has its seat in some active layer other than the metal and that it is either built up or broken down by the heating. If it were a case of gradual removal the curves of Robinson would be followed in the inverse order. The lack of symmetry of the elevations of the curves about their maximum ordinates might make possible a decision as to which of the last two assumptions is the tenable one. It may be more than a coincidence that the accepted value, on the theory of the transition layer, of the thickness of adsorbed gas films is of the same order of magnitude as the thickness of platinum film for maximum photo-electric current: namely, 10^{-7} cm.

SUMMARY.

A spectroscopic study has been made of the gases emitted by silver, gold, nickel, palladium and platinum at various temperatures between that of the room and fusion. Simultaneous measurements were made (after cooling of the metal) of the photoelectric emission. They are plotted against heating currents instead of temperatures. Nickel, palladium and platinum were found to emit carbon gases or oxygen, only, in the intervals of high photo-sensitiveness. Hydrogen is emitted elsewhere. Silver and gold give off hydrogen at all heating currents, but in intervals of high photo-sensitiveness the predominatimg part of the mixture of gases is one giving the carbon spectrum.

The effects of pure gases on the cleaned metals were looked into for two reasons. The matter is of interest in itself and it was hoped to imitate the curves obtained during the original cleaning. A mixture of hydrogen and oxygen gives fair imitation for the three metals on which it was tried; silver, palladium and platinum. Oxygen alone gives a good imitation of nickel. Carbon dioxide is of no influence on the metals unless it is alone. This gas, and also nitrogen and possibly hydrogen, is incapable of protecting the metals from the action of some residual gas or vapor in the cell. By a comparison of curves taken immediately on cleaning, without gas treatment, or after the metals remained in vacua for several hours; the active residual gas was shown to be either carbon

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[1] Loc. cit.

monoxide or methane. It is only in gold that constancy of photosensitiveness is approached in the "immediate" curves. With platinum the variations are enormous. Cyanogen and illuminating gas introduced novel features into the curves.

Charging electrolytically, or glowing, gave the same types of curves, generally, as mere contact with gas. Metals heated in a gas are usually photo-electrically stable with regard to further heating. Heating in flames, plain or colored, gives the hydrogen-oxygen type of curve. Colored flames leave an easily removable activity. The presence of lime or a salt of calcium gives characteristic heating current-photo current curves.

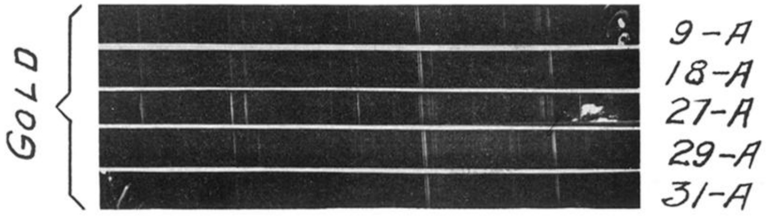
No definite theory is proposed, but the possibilities are considered on the bases of:

1. The primary valence theory of adsorption,
2. The transition layer theory of adsorption,
3. Solution of gas in metal.
4. Chemical combination of gas and metal,
5. Photo-electrically active layer being built up or destroyed by the heating.

The experimental means of deciding among some of these are outlined.

This work was suggested and its progress directed by Professor E. P. Lewis. It gives me pleasure to acknowledge his aid and constant encouragement.

UNIVERSITY OF CALIFORNIA,
March, 1918.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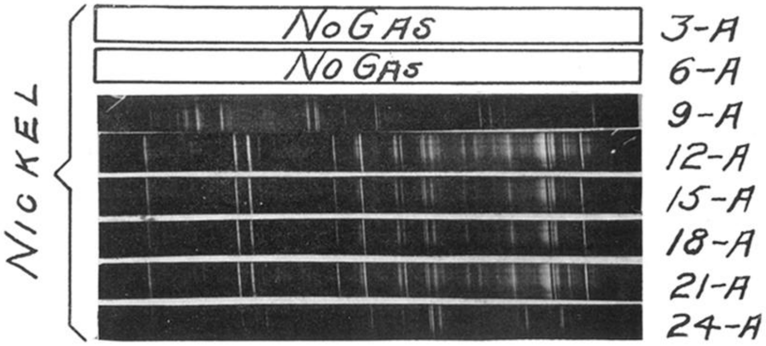
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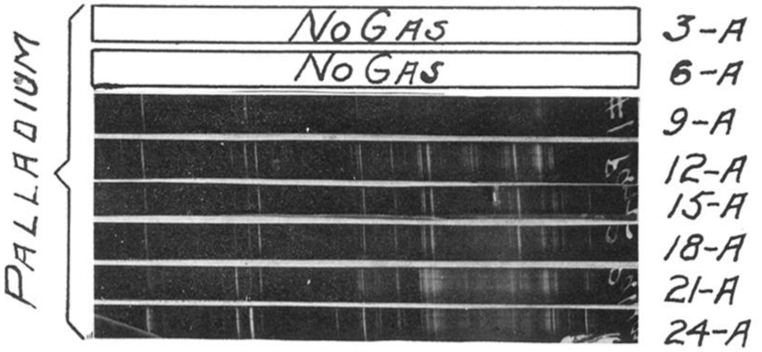
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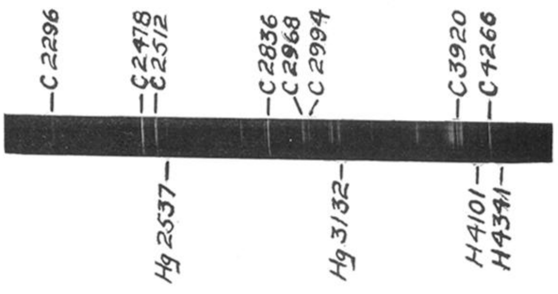
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