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On the Occlusion of Hydrogen and Oxygen by Palladium

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III. *On the Occlusion of Hydrogen and Oxygen by Palladium.*

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Contents.

I. *Introduction.*

Since the discovery by Graham ('Phil. Trans.,' 1866, p. 399, also 'Graham's Researches,' p. 235), that palladium possesses the property of occluding or absorbing large quantities of hydrogen, chemical literature has been enriched by various contributions to our knowledge of this interesting phenomenon. To mention only a few of these, some of which will later on be considered in detail, we have the results of investigations on the change of volume undergone by palladium on the occlusion of hydrogen, the density of the occluded hydrogen, the heat changes which take place, and the pressure of "palladium hydrogen" at different temperatures, &c.

The solution of hydrogen in, or the combination of hydrogen with, palladium, which we may be permitted provisionally to term palladium hydrogen, is now often used in laboratories as a convenient source of pure hydrogen; and finely divided palladium, on account of the facility with which it absorbs hydrogen, is also extensively employed in gas analysis. Hydrogen, occluded by palladium, may conveniently be weighed as palladium hydrogen, and recourse was had by Keiser

('Am. Chem. Journ.,' vol. 10, p. 249) to this method of weighing hydrogen in one of the most delicate of chemical operations, viz., that of atomic weight determination.

Any addition to our knowledge of this substance may therefore be expected to be of interest. It will readily be admitted that the phenomenon of occlusion is one which requires further elucidation, and in submitting the present communication to the Society we hope that the additional work we now bring forward will not only be of interest for its own sake, but that it will finally assist us in arriving at a definite decision with regard to the nature of occlusion.

In previous communications ('Phil. Trans.,' A, vol. 186, p. 657, and A, vol. 190, p. 129) we discussed the relations of platinum black to oxygen, hydrogen, and other gases, and on p. 152 of the latter paper we pointed out that until the relation of the palladium to the hydrogen in the comparatively well defined substance palladium hydrogen was ascertained, there was little hope of solving the corresponding problem for the less well defined substance platinum hydrogen.

We therefore turned our attention to the general behaviour of palladium to oxygen and hydrogen, and now give an account of our work on the subject, which includes measurements of the heat evolved on the absorption of these gases, and a comparative study of the occlusion of hydrogen by palladium in different states of aggregation.

II. *Preparation of the Palladium.*

The palladium employed in these experiments was in the form of (*a*) black, (*b*) sponge, and (*c*) foil.

Palladium black.—Some strips of metallic palladium, which were said to have been prepared by WOLLASTON, were purified in the following manner:—After dissolving in *aqua regia* and evaporating several times successively with water and hydrochloric acid, the solution was treated with excess of ammonia, and filtered. From the filtrate pure palladosamine chloride was precipitated by leading a stream of hydrochloric acid gas through it. This was filtered off, washed with strong hydrochloric acid, dried, and ignited. The residue, consisting of palladium sponge, was then again brought into solution by digesting with aqueous hydrochloric acid through which a current of chlorine gas was led. After evaporating, to get rid of the excess of hydrochloric acid and chlorine, the solution of palladium was neutralized with sodium carbonate, and slowly poured into a boiling, very dilute solution containing excess of sodium formate. The palladium black, precipitated in this way, was then repeatedly boiled out with distilled water until free from alkalis and alkaline chlorides, and dried at 100° C.

Palladium sponge.—The palladium sponge employed in the course of these experiments was prepared by fully charging the necessary quantity of palladium black with hydrogen, and then igniting at a red heat *in vacuo*, since simple ignition of palladium black in the air or *in vacuo*, unless conducted at an extremely high temperature, is insufficient to remove the oxygen initially contained in it.

Palladium foil.—A portion of thin foil was procured from Messrs. JOHNSON and MATTHEY, and was guaranteed to contain over 99 per cent. of palladium. The special treatment to which this was subjected will be described in Section VI.

III. *Density of Palladium.*

It has always been customary, in stating the quantity of hydrogen occluded by palladium, to express the result as so many volumes of hydrogen occluded by unit volume of palladium.

This makes a knowledge of the density of palladium necessary.

The density of the foil employed was found to be 12·1, whilst a direct determination of the density of palladium black, dried at 100° C. in a specially constructed pyknometer, gave the value 10·6. This refers to palladium black prepared as described. An analysis of the black soon after it was dried showed that it contained 0·72 per cent. of water and 1·65 per cent. of oxygen, existing probably as oxide. If we make an allowance for this amount of water contained in the black the density rises to 11·4.

The palladium black used for the density determination was the remainder (over 5 grams) contained in a bottle which had been frequently opened during about four months, and which in all probability had absorbed more water. If we assume that the percentage of water had gone up from 0·72 per cent. to 1 per cent. during the four months, then the density of dry palladium black would become 11·8. No allowance, however, has been made for the fact that the palladium black contained oxygen, which would also tend to lower the density.

Since the knowledge of the density was only essential for the purpose of translating the actual quantity of hydrogen occluded into the number of volumes of hydrogen occluded by unit volume of palladium, we have thought it better, in view of the above circumstances and of the fact that the determination of the density of a fine powder like palladium black is not at all easy, to adopt, for comparative purposes, the value 12·0 as the density of palladium in its three states of aggregation, viz., black, sponge, and foil. As the actual measurements are always given in addition, this assumption ought not to give rise to any error, and is to a certain extent justified by the fact that, under proper conditions, the number of volumes of hydrogen occluded by unit volume of the different varieties of palladium remains practically the same.

IV. *Analysis of Palladium Black.*

Before beginning any extended experiments with palladium black a preliminary examination was made. From the fact that platinum black prepared in the same way invariably contains oxygen, it was thought that palladium black would also contain oxygen. On igniting 1·5650 gram palladium black in a hard glass tube *in vacuo*, however, only 0·33 cub. centim. oxygen and 0·56 cub. centim. carbon dioxide were extracted. This proves that the oxygen, if any be present, is more firmly retained by palladium than by platinum.

Another portion of palladium black, weighing 1·9795 gram, was placed in a hard glass bulb tube, one end of which was attached to a weighed U-tube containing P_2O_5, and thence to the pump, whilst the other end was connected with an apparatus supplying pure dry hydrogen. On ignition *in vacuo* 0·0142 gram H_2O was collected in the U-tube. This corresponds to the presence of 0·72 per cent. of water. No oxygen was given off, but on passing hydrogen over the sponge remaining in the hard glass tube 0·0326 gram H_2O was obtained. The palladium black therefore contained 1·65 per cent. of oxygen, corresponding to 23·69 per cent. Pd_2O, or 12·69 per cent. PdO. If we assume that the oxygen exists as PdO, and if we estimate the pure palladium by difference, we get for the analysis of palladium black :—

Palladium	86·59	per cent. ;	
Palladium oxide (PdO) . .	12·69	,,	= 1·65 per cent. O_2 ;
Water	0·72	,,	

From the weight of water formed, it follows that the palladium black contained 22·82 cub. centims., or 138 volumes of oxygen. The oxygen initially present in palladium black was also determined in another way.

Palladium black was fully charged with hydrogen, a portion of which was really occluded, whilst the remainder formed water with the oxygen pre-existing in the black. The occluded hydrogen is easily determined by extracting at a red heat *in vacuo*, and half the difference between the volume of hydrogen used and that pumped off represents the volume of oxygen initially present. In this way it was found (see table, p. 125) that the palladium black contained 140, 141, and 143 volumes of oxygen, whilst the gravimetric determination indicated the presence of 138 volumes.

Pure palladium sponge is almost white, whilst that obtained by the direct ignition of palladium black *in vacuo* is much darker in colour owing to the presence of oxygen or oxide in it.

V. *Absorption of Oxygen by Palladium.*

We have already shown ('Phil. Trans.,' A, 1895, vol. 186, p. 682) that when platinum black is heated in an atmosphere of oxygen, kept approximately at ordinary pressure, absorption of oxygen takes place until the temperature rises to about 360° C., when the gas is again expelled. If this is really a process of oxidation, then, since palladium is usually regarded as a more easily oxidisable metal, it is to be inferred that palladium black will behave in the same way, although perhaps to a greater extent.

In the first experiment 3·519 grams of palladium black were heated in an atmosphere of oxygen in an apparatus similar to that employed for the corresponding experiments with platinum. The following results show that oxygen was steadily absorbed :—

Heated for	Oxygen absorbed.	
	cub. centims.	volumes.
2 hours at 132°	3·29	11·2
6 " 184°	18·18	62·0
6 " 237°	33·73	115·1
6 " 280°	46·18	157·6
Total	101·38	345·9

Up to 280° C. the total quantity of oxygen absorbed, viz., 101·38 cub. centims. = 0·1450 gram, is more than half the quantity of oxygen (0·2656 gram) necessary to form the compound Pd_2O. Owing to an accident, which prevented the experiment being carried further, a new portion of palladium black was taken, and the heating in oxygen started at 280° C. The following results were obtained :—

OXYGEN Absorbed by Palladium at High Temperatures.

Palladium black used, 2·8100 grams = 0·234 cub. centim.			
Heated for	Oxygen absorbed.		
	cub. centims.	volumes.	gram.
12 hours at 280° C.	87·59	374	0·1253
5 " 280° C.	6·42	27	0·0092
1½ " 360° C.	16·28	70	0·0233
3 " 444° C.	18·21	78	0·0260
3 " 444° C.	17·79	76	0·0254
2 " 444° C.	10·68	47	0·0153
1½ " 600° C.	9·17	39	0·0131
3 " a red heat (naked flame)	60·34	258	0·0863
Total	226·48	969	0·3239

The quantity of oxygen theoretically necessary for the formation of the oxide Pd_2O is 0·2121 gram, and it will be observed that the oxygen actually absorbed exceeds this quantity. There is no reason to suppose that the absorption of oxygen had ceased after the experimental tube had been heated for three hours in the naked flame. The experiment was stopped at this stage, however, in order to see whether the excess of oxygen over and above that required for the formation of Pd_2O could be removed *in vacuo* at any intermediate temperature.

After being placed in communication with the pump the experimental tube was then exposed to gradually increasing temperatures, and finally to as high a temperature as the hard glass tube would stand without collapsing.

Only a few bubbles of gas (about 1 cub. centim.) could be extracted, and hence it appears that if either or both of the oxides Pd_2O and PdO are formed, they must be stable *in vacuo* at a dull red heat. The substance formed during the absorption of oxygen has a dark brown colour, has lost all the appearance of palladium sponge, and is, without doubt, an oxide or mixture of oxides.

According to WILM ('Berichte,' 1882, p. 2225), the sub-oxide of palladium, Pd_2O, may be prepared by heating the sponge in a current of air until it attains a constant weight. If this is so, it is curious that we have not been able to observe any discontinuity in the absorption of oxygen, and we are inclined to think that palladium sponge, if heated for a sufficiently long time in a current of air, should yield not the sub-oxide, but palladium oxide, PdO.

We have already seen that palladium black, prepared in the way described, contains about 140 volumes, or 1·65 per cent. of oxygen, and the fact that the substance was dried at 100° C. probably accounts for the presence of a certain quantity of this oxygen. In connection with the calorimetric experiments to be described later on, it was of interest to us to know how much oxygen palladium black, rendered free from oxygen, would absorb directly at 0° or at the ordinary temperature. We found it impossible to remove the oxygen without converting the black into sponge, but the required information was obtained in the following way :—

The sample of palladium black was fully charged up with hydrogen, whereby all the oxygen was removed as water. As will be seen presently, the bulk (over 90 per cent.) of the occluded hydrogen was next extracted by exhausting at 100° C. To the palladium black containing only a comparatively small quantity of hydrogen, oxygen was then admitted, in the first instance very slowly, whilst the experimental tube was kept cold by immersion in melting ice, and in the second rapidly, whilst the tube was simply exposed to the atmosphere. Of course a portion of the oxygen formed water with the residual hydrogen, the rest being absorbed, in the first case without appreciable rise of temperature, and in the second with considerable rise of temperature. The absorbed oxygen was then determined in both specimens by charging up fully with hydrogen and exhausting at a red heat. It was found that about 40 volumes and 120 volumes respectively of oxygen were absorbed.

At 0° C., therefore, the absorptive power of palladium black for oxygen is considerably lessened.

It will readily be admitted that the absorption of oxygen by palladium black is really a process of oxidation, and although palladium and platinum belong to different sub-divisions of the platinum group of metals, we think the absorption of oxygen by platinum black may also best be explained as a superficial oxidation, the chief difference being that the oxide of platinum decomposes or dissociates at a lower temperature than the corresponding oxide of palladium.

VI. *Observations on the Occlusion of Hydrogen by Palladium Black, Sponge, and Foil.*

A series of experiments was next undertaken with the object of comparing the relative occlusive power of palladium in the form of (*a*) black, (*b*) sponge, and (*c*) foil for hydrogen, and investigating the behaviour of the substances produced. This was especially necessary in the case of palladium foil or wire, since the statements of different observers are at considerable variance with each other. Whilst most are agreed that palladium in the compact state readily occludes the maximum quantity of hydrogen when charged electrolytically, there are many cases on record in which the compact metal only occludes a relatively small quantity of hydrogen when it is simply exposed or ignited in the gas.

a. *Palladium Black.*—1·619 gram = 0·135 cub. centim. palladium black was charged with pure dry hydrogen in an apparatus similar to that employed for the corresponding experiments with platinum black ('Phil. Trans.,' A, 1895, vol. 186, pp. 668 and 687). Altogether 152·76 cub. centims. (0° and 760 millims.) = 1131 volumes of hydrogen were absorbed, the greater portion of which was taken up almost instantaneously.

From the experiments already described, it is to be expected that a certain fraction of the total hydrogen absorbed formed water with the oxygen pre-existing in the palladium black. In order to determine the quantity of hydrogen which was really occluded and how much was given off *in vacuo* at different temperatures, the experimental tube was exhausted first at the ordinary temperature, then at higher temperatures, and finally at a red heat. The results are given in the following table :—

Palladium black used, 1·619 gram = 0·135 cub. centim. Total H_2 absorbed, 152·76 cub. centims. = 1131 volumes.		
Temperature.	Occluded hydrogen pumped off.	
° C.	cub. centims.	volumes.
20	105·72	783·2
100	2·41	17·8
184	2·27	16·8
280	3·29	24·4
444	1·32	9·8
700 (?)	0·21	1·6
Total . . .	115·22	853·6

The difference between the total hydrogen absorbed and that extracted at a dull red heat *in vacuo* corresponds to the presence of 18·77 cub. centims., or 139·1 volumes, of oxygen in the palladium black. Since this volumetric estimation of the amount of absorbed oxygen is in good agreement with the direct gravimetric determination, viz., 138 volumes, we are justified in concluding that 115·22 cub. centims., or 853·6 volumes, is the quantity of hydrogen really occluded.

It will be observed that practically the whole of the occluded hydrogen was extracted at 444°, and that about 92 per cent. of it can be pumped off at the ordinary temperature. The last traces of the hydrogen given off at the ordinary temperature come off very slowly, so that the pumping requires to be continued for a day, or longer.

It was noticed that the palladium black contracts and passes into sponge above 184° C.

This result, viz., that palladium black occludes about 854* volumes of hydrogen, was confirmed by additional experiments (*v.* Table, p. 125), in which 860*, 868*, and 868* volumes were occluded.

b. *Palladium Sponge.*—The pure palladium sponge remaining behind in the experimental tube after the preceding experiment was completed was charged with hydrogen. 112·4 cub. centims. = 833* volumes were occluded. Of this 111·5 cub. centims., or 826·1 volumes, representing about 99 per cent. of the whole, were pumped off at the ordinary temperature, whilst on heating to *redness* 1·4 cub. centim., or 10·4 volumes, were extracted. It would appear, therefore, from this experiment that more hydrogen can be removed from palladium sponge than from palladium black at the ordinary temperature.

This does not agree with GRAHAM's observation ('Researches,' p. 287) that "in the pulverulent spongy state palladium took up 655 volumes of hydrogen, and so charged, it gave off no gas *in vacuo* at the ordinary temperature, nor till its temperature was raised to nearly 100°."

c. *Palladium Foil.*—The palladium foil employed weighed 1·333 gram, and was about 0·025 millim. thick. It had been prepared by rolling out sponge, and was said to contain over 99 per cent. of palladium.

Before being introduced into the experimental tube it was boiled in caustic potash solution, washed, and dried between filter paper.

On ignition *in vacuo* a small quantity of gas, which was not examined, was given off. After cooling down to the ordinary temperature again, hydrogen was admitted, but apparently none was occluded. The palladium was therefore ignited in the hydrogen and allowed to cool down slowly. Next day it was found that only 29 volumes had been occluded. Practically none of this could be extracted *in vacuo* at the ordinary temperature, but on ignition 28 volumes were pumped out.

The result of this experiment, therefore, goes to show that the occlusion of hydrogen by new compact palladium foil is thus either (1) very small, or (2) very slow.

* A slight correction must be applied to these numbers, the nature of which is explained on p. 120, and the corrected values will be found in the Table on p. 121.

When palladium foil is charged electrolytically with hydrogen it undergoes a considerable increase in volume, as has been pointed out by GRAHAM, DEWAR, THOMA, and others, and when discharged it again contracts, and it is said that its volume becomes less than the original volume. In order to see whether the occlusive power of the foil was altered by successive expansion and contraction, it was charged successively and alternately with hydrogen and oxygen in a voltaic cell. After exhaustion at a red heat *in vacuo*, hydrogen was admitted at the ordinary temperature. The following results were obtained :—

On first admission of hydrogen .	0·3 cub. centim.	=	2·7	volumes were occluded;
After gently heating for two hours	3·6 ,,	=	32·2	,, ,, ,,
After eighteen hours at ordinary temperature	0·3 ,,	=	2·7	,, ,, ,,

Altogether, therefore, 4·2 cub. centims., or 37·6 volumes, of hydrogen were occluded. The occlusive power is thus not much greater than before. If the compactness of the metal has anything to do with the rate of occlusion, this result is what might have been anticipated, since on charging electrolytically with hydrogen and then discharging the volume of the metal becomes less, and presumably the degree of compactness greater.

There can be little doubt that the phenomenon of occlusion consists first of the *solution* or *combination* of the gas in the outer skin of the metal, and then of *diffusion* inwards towards the centre.

In the case of compact foil, produced by the welding together of particles of sponge, the hydrogen is possibly condensed, dissolved, or combined in the two chief outer surfaces of the foil, and then diffuses inwards in both directions through half its thickness. In the case of palladium sponge or black, however, the surface itself is very much greater, and the diameter or radius of the individual particles probably very much less than the thickness of the foil; and consequently it would seem that with palladium sponge we have to deal chiefly with the rate of solution, and that we are less concerned with the factor of diffusion or rate of diffusion.

Hence, if we could by any possible treatment so change new compact palladium foil that it becomes spongy in texture, it is to be expected that it would behave more nearly like palladium sponge as regards the amount of hydrogen occluded and the rate at which occlusion takes place.

It is well known that when copper is oxidised and then reduced it becomes spongy. Now, a favourite device for cleaning platinum and palladium goods is by ignition in the blowpipe flame. Palladium, however, differs from platinum inasmuch as it is more easily oxidised. At a still higher temperature (higher than can conveniently be maintained in an evacuated hard glass tube), it is again reduced to metal. By repeatedly igniting palladium foil in this way it probably acquires a more or less spongy nature, due to the transition through the state of oxide, and consequently we should expect it to behave more like the sponge.

Most of the palladium employed by other observers has probably been subjected to this treatment, which possibly explains the readiness with which in most instances it takes up hydrogen. There is also evidence, from other sources, that new palladium foil possesses a lower absorption power for hydrogen. For example, a portion of new palladium foil, examined by GRAHAM ('Researches,' p. 268), and believed to be from *fused* metal, occluded only 68 volumes of hydrogen. This is ascribed by GRAHAM to the fact that the metal had been fused. "An inferior absorbing power for hydrogen appears to be connected in both platinum and palladium with the fusion of the metal." GRAHAM'S explanation is quite consistent with the view here put forward, for the fusion of the metal would simply produce (only, perhaps, in a more perfect way) the same effect as a thorough welding or rolling.

The foil examined by us had not been fused, but it persistently refused to occlude hydrogen in any quantity.

After it had been submitted to the preceding operations it was ignited several times in the blowpipe flame, rolled up, reignited, and introduced hot into the experimental tube.

On now admitting hydrogen at the ordinary temperature about 33 volumes were immediately absorbed. When the experimental tube was warmed by a naked BUNSEN flame an additional quantity of hydrogen, amounting to over 100 volumes, was suddenly occluded. On heating more strongly this gas was expelled and again reabsorbed on cooling. The experimental tube was now placed in a water bath. When the temperature reached 88°–90° C. absorption again began and continued slowly at 100° C., beginning at the rate of about 1 cub. centim., or 9 volumes, per minute and gradually diminishing. In an hour and a half at 100° C. about 500 additional volumes had been occluded, and on standing overnight at the ordinary temperature only a very little, if any, hydrogen was absorbed.

Next day an oil bath was substituted for the water bath, and the temperature was gradually raised above 100° C. Absorption again went on until 130° was reached, when the occluded gas began to be expelled. The temperature was therefore lowered to 120°. Absorption continued for two hours, and then appeared to diminish. By allowing the temperature of the bath to fall to 100° absorption again took place, and continued for another hour. The apparatus was now allowed to remain for 44 hours at the ordinary temperature, when we were surprised to find that a further absorption of about 100 volumes had taken place.

It would thus appear that after the occlusion of hydrogen has made a fair start, or when the palladium has been largely converted into palladium hydrogen, a further absorption is able to go on at the ordinary temperature. This may be due to the change in texture of the palladium caused by ruptures between the particles of the metal produced by the expansion during the first part of the charging. GRAHAM (*loc. cit.*, p. 267) remarks, "The foil was much crumpled and rather friable after repeated use."

The fact that increase of temperature is necessary during the first part of the absorption is to be ascribed not to an increase in the solubility of the hydrogen, but to a more rapid diffusion, throughout the mass of the metal, of such hydrogen as can be retained at that particular temperature. The meaning of this will be rendered clearer by reference to DEVILLE and TROOST'S well-known experiment on the passage of hydrogen through a red-hot platinum tube, or to the similar passage of hydrogen through a palladium tube above 237° C. (*cf.* RAMSAY, 'Phil. Mag.,' August, 1894, p. 206). Now platinum and palladium at this high temperature can only retain under atmospheric pressure* a very minute quantity of hydrogen, but, minute as it is, it can *diffuse* with great readiness through the hot metal, its place being immediately taken by fresh hydrogen. At moderately high temperatures therefore, when palladium can still absorb a considerable quantity of hydrogen, we should expect a more rapid diffusion through, or permeation of, the foil, and consequently the production of a spongy or fissured mass, caused by expansion on the occlusion of just as much hydrogen as can be retained at this temperature, so that on cooling down to the ordinary temperature the foil ought to behave more nearly like palladium sponge.

At this stage an exact measurement of the total quantity of hydrogen absorbed was made, and it was found that 94·50 cub. centims., or 851 volumes, had been taken up by the palladium foil.

That the absorption at 100° was complete was shown by the fact that on raising the temperature to 100° C. about 100 volumes of gas were expelled, and of this about three-quarters was reabsorbed on cooling down to the ordinary temperature, whilst the remainder, along with seven additional volumes, was occluded on standing for eighteen hours. The final measurement showed that 95·18 cub. centims., or 858 volumes, of hydrogen had been absorbed.

Just as palladium foil which has been rendered more or less spongy in texture requires a considerable time for the absorption of its quantum of hydrogen, so also it gives off its occluded gas extremely slowly *in vacuo* at the ordinary temperature. On applying the pump a practically complete vacuum was produced in a few minutes, when it was found that only 0·57 cub. centim., or five volumes, had been removed. Hydrogen was, however, given off very slowly, for in another hour 2·14 cub. centims., or nineteen volumes, were extracted. The results are contained in the following table, which shows that nearly the whole of the hydrogen is given off easily and rapidly at 100° C. *in vacuo*. There is a difference of twelve volumes between the total hydrogen absorbed and the total hydrogen extracted or occluded. This may be due to (1) experimental error, (2) all the hydrogen may not be extracted at a red

* The most recent work on the subject by Professor DEWAR ('Proc. Chem. Soc.,' 1897, No. 183, 192) shows that a rod of palladium is still capable of occluding about 300 volumes of hydrogen, under a pressure of 100–120 atmospheres, at a temperature of 500° C.

heat, or (3) the presence of a film of oxide on the foil. Of these (2) is unlikely, so that the deficit may be regarded as due to (1) and (3), and probably chiefly to (3).

Palladium foil used, 1·333 gram = 0·111 cub. centim.
Total H_2 absorbed, 95·18 cub. centims. = 858 volumes.

Temperature.	Occluded hydrogen pumped off.	
	cub. centims.	volumes.
20° (rapidly)	0·57	5
20° (in one hour)	2·14	19
100°	90·77	818
700° (red heat)	0·39	4
Total	93·87	846

After all the hydrogen had been extracted from the foil, it was again charged with hydrogen. A slow absorption went on, and this was promoted at the beginning by warming. On opening the tube and bringing the foil, partially charged with hydrogen, into contact with the air, it became distinctly warm to the touch, and after standing for a short time drops of water were deposited on the walls of the tube.

Under proper conditions, therefore, as above set forth, a sample of new palladium foil which initially would only occlude a few volumes of hydrogen may be made to occlude 846, or roughly 850, volumes, that is approximately the same quantity of hydrogen as palladium black or sponge.

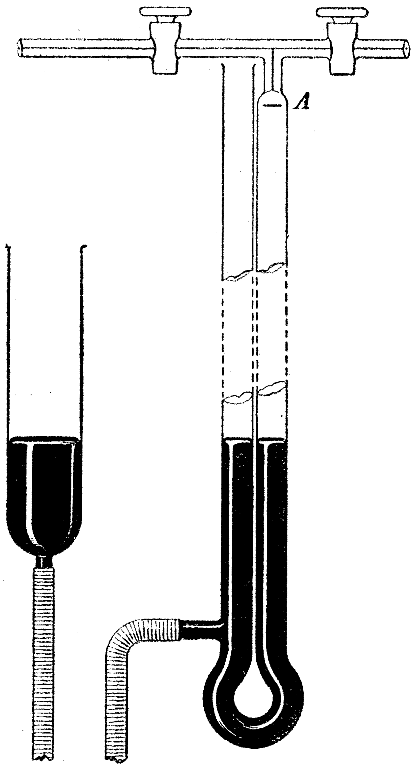
New palladium foil, or even fused palladium, if left for a sufficiently long time (possibly months or years) in an atmosphere of hydrogen at the ordinary temperature, would probably absorb the full quantity of hydrogen, the effect of gentle warming being to accelerate (as above) the diffusion of the hydrogen from the fully charged outer skin of the metal towards the centre.

A few additional experiments on the behaviour of palladium to other gases may conveniently be recorded here. Some palladium black was fully charged with hydrogen, and from this as much hydrogen as possible was extracted at 100°. On now admitting sulphur dioxide only about 90 volumes were taken up, in place of about 800 volumes of hydrogen removed. Palladium sponge when treated with sulphur dioxide absorbed only two volumes. About seventeen volumes of carbon monoxide were occluded by palladium sponge.

Palladium black and sponge, like platinum sponge, cause a jet of hydrogen to ignite. When hydrogen was led over palladium black which had absorbed more oxygen at a high temperature, it glowed brightly. A specimen of ordinary palladium black, however, did not glow on passing hydrogen over it, although it became very hot. Apparently it was not itself sufficiently rich in oxygen. Palladium black or sponge charged with hydrogen glows like pyrophoric iron on being shaken out into the air.

VII. *The Heat of Occlusion of Hydrogen by Palladium Black.*

The determination of the heat of occlusion of hydrogen by palladium black was made in the ice calorimeter already described by us ('Phil. Trans.,' A, 1897, vol. 190, p. 131), and it may be interesting to note that during the course of these investigations the temperature of the room in which the calorimeter was placed varied between 20°–24° C. The experiments were made in a manner precisely similar to the corresponding series with platinum black, the only essential difference being that a constant volume manometer was attached to the experimental tube.



A constant volume manometer was constructed, as shown in the accompanying figure. This form was chosen for two reasons. In the first place, it obviated the necessity of calibration. The capacity of the capillary tubing between the two taps and the mark at the point A was determined once for all and added to that of the experimental tube. During the course of the experiments the mercury in the right limb was always kept *near* the mark A, and during an actual measurement of pressure exactly *at* the mark. The second and chief reason for selecting this form of manometer, however, was that the main bulk of the gas in the experimental tube was at 0° C., whilst the projecting portion was at atmospheric temperature, and in the case of an ordinary manometer it would have been very difficult to estimate the average temperature of the projecting volume of gas, which would have been considerable, since capillary manometers are unreliable.

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Before being used the manometer was exhausted and found to give readings practically identical with those of the barometer at the time.

A quantity of palladium black was introduced into the experimental tube, the capacity of which was determined. It was then fully charged with hydrogen and exhausted as completely as possible at 100° C. before being placed in the calorimeter, when it was sealed on to the burette, furnishing pure hydrogen, the pump, and the manometer.

After the experimental tube had remained several days in the calorimeter it was found, by making connection with the manometer, that the internal pressure was practically zero. The reduced readings of the barometer and manometer were 757·5 millims. and 757·7 millims. respectively. It was estimated that the quantity of palladium black in the calorimeter was now in a position to occlude over 110 cub. centims. of hydrogen, which was admitted in four separate fractions.

In estimating the amount of hydrogen actually occluded in each case, account was taken of the unabsorbed hydrogen existing in the experimental tube before and after the admission of the gas from the burette. The quantity of unabsorbed hydrogen was ascertained from the known capacity of the apparatus (6·30 cub. centims.), its temperature, viz., 0° C., and the pressure indicated by the manometer.

The deflection of the mercury meniscus in the capillary tube of the calorimeter was corrected, when necessary, for the slight errors due to the fact that the bore of the tube was not quite uniform. The results are given below in tabular form.

HEAT of Occlusion of Hydrogen by Palladium Black.

Palladium black used, 1·6658 gram.						
Experiment.	Hydrogen occluded.		Pressure of palladium hydrogen.	Deflection.	Heat produced, K.=100 g. cal.	Heat produced per gram of hydrogen occluded.
	cub. centims.	gram.	millims.	millims.		K.
I.	37·26	0·003353	8·1	147·5	+0·1553	+46·32
II.	35·16	0·003164	13·1	139·0	0·1464	46·27
III.	32·40	0·002916	106·6	129·4	0·1362	46·72
IV.	6·79	0·000611	757·6	27·6	0·0291	47·56
V.	−22·72	−0·002045	4·5	− 88·4	−0·0931	−45·52

Altogether 111·61 cub. centims., or 803 volumes, of hydrogen were occluded in addition to that which was already present in the palladium, and which could not be removed *in vacuo* at 100°. From previous experiments (see table, p. 111) this probably amounted to a little over 50 volumes.

It is evident from the last column of the table that the heat evolved per gram of hydrogen occluded remains the same for the different fractions.

The mean of the four experiments is 46·72 K., and if we exclude the last, in which experimental errors have a greater influence owing to the smallness of the quantity of hydrogen occluded, the mean of the three principal results is + 46·44 K., and the deviation from this mean in the case of the fourth result is only 0·6 per cent.

The value + 46·44 K. for the heat evolved per gram of hydrogen occluded may safely be taken as correct within 1 per cent.

In Experiment V. a portion of the hydrogen which had been occluded was exhausted by means of the pump, giving the number 45·5 K. *absorbed* per gram of hydrogen *removed*. The hydrogen comes off so slowly at 0° C. that the experiment could not be continued. The result does not differ very much from those already obtained, and no doubt the conditions under which the experiment was made account largely for the difference. In experimenting with the ice calorimeter it is essential, in order to obtain an accurate measurement of the deflection, that the normal creepage of the instrument should be in the same direction as the deflection to be measured. In this case, however, the two were opposed to each other. In the particular instrument with which we have worked, there was generally a slow creepage inwards, due to the slow melting of the ice. In any serious attempt, therefore, to measure the amount of heat absorbed, it would be advisable to alter the melting point of the ice in the interior of the calorimeter by increasing or diminishing the pressure at the open end of the capillary tube until the creepage was either entirely suspended, or, at least, in the same sense as the deflection to be measured.

FAVRE, by means of his mercury calorimeter ('Comptes Rend.,' vol. 78, p. 1262), determined the heat evolved on the occlusion of hydrogen by palladium sponge, and obtained numbers varying from 202·7 K. to 38·9 K. The results which exceed 60 K., however, were only obtained for the first fractions of hydrogen admitted, and were obviously due, as FAVRE himself recognised, to the simultaneous occurrence of a second reaction, viz., the formation of water from oxide of palladium.

If we exclude four* of FAVRE's experiments, in which the result is greater than 60 K., then the general mean of the twenty-five remaining experiments, varying between 60 K. and 38·9 K., is 48·6 K. per gram of hydrogen occluded, a result which is approximately the same as that found by us, viz., 46·4 K. In another independent series of experiments ('Comptes Rend.,' vol. 68, p. 1306) FAVRE estimated the heat of occlusion of hydrogen at 41·6 K. from the difference between the quantities of heat evolved when an ordinary Smee cell was placed in the calorimeter (*i.e.*, when the hydrogen was allowed to escape) and when in the same cell

* Three of the four are the first members in a series of seventeen experiments, whilst the fourth is the first of another series of eleven experiments.

the platinum plate was replaced by palladium, so that the heat evolved on the occlusion of the hydrogen was also included.

Independent of direct measurement in the calorimeter, the heat of a reaction can be calculated, as was first shown by HORSTMANN ('Berichte,' 1869, vol. 2, p. 137), by an application of the second law of thermodynamics to the dissociation pressures of the substance at different temperatures. From measurements of the dissociation pressures of palladium hydrogen by TROOST and HAUTEFEUILLE ('Ann. Chim. Phys.,' (5) vol. 2, p. 279), MOUTIER ('Comptes Rend.,' vol. 79, p. 1242) calculated that the heat of occlusion of hydrogen by palladium at 20° C. was 41·5 K. per gram, and more recently DEWAR ('Proc. Chem. Soc.,' 1897, No. 183, p. 197) obtained, from similar measurements by ROOZEBOOM (HOITSEMA, 'Zeitschr. Physikal. Chem.,' 1895, vol. 17, p. 1), the value (45·61 + 0·2378 T.) K. At 0° C. (273° abs.), therefore, the heat evolved per gram of hydrogen occluded becomes 46·26 K., which agrees very closely with the value, 46·44, found by us. The magnitude which is directly measured in the calorimeter, however, represents the true heat of the reaction plus the heat corresponding to the work done by the atmosphere, viz., 2·7 K.,* and hence the true heat of occlusion of hydrogen by palladium black is only 46·4 − 2·7 = 43·7 K. per gram of hydrogen.

VIII. *Investigation of the Ratio Palladium : Hydrogen.*

From the analysis of palladium black (*v.* p. 108) it follows that the black as prepared contained 97·63 per cent. palladium, the remainder consisting of 1·65 per cent. oxygen and 0·72 per cent. water. Hence, in calculating the ratio of the number of atoms of palladium to the number of atoms of hydrogen in palladium fully charged with hydrogen, we ought to reduce the weighed amount of palladium black to palladium metal *per se.* Strictly speaking, this ought also to be done in expressing the number of volumes of hydrogen occluded by unit volume of palladium existing in the substance we call palladium black.

The following table contains the atomic ratio of palladium to hydrogen for fully charged palladium black, sponge, and foil (the atomic weight of palladium being taken as 107), and also the corrected number of volumes of hydrogen occluded by unit volume of palladium :—

* *V.* p. 123.

	Palladium / Hydrogen.	Volumes of Hydrogen occluded.
Palladium black	1·42	873
„ „ I.*	1·41	881
„ „ II.*	1.40	889
„ „ III.*	1·40	889
„ sponge	1·46	852
„ foil	1·47	846
„ wire I. (GRAHAM) . . .	1·37	912 (936)
„ „ II. „ . . .	1·46	846 (867)
„ „ III. „ . . .	1·44	859 (888)
„ metal (DEWAR) . . .	1·47	847

We have also included in the table the corresponding values which we have calculated from three experiments by GRAHAM ('Researches,' p. 291) and from an experiment on a larger scale by DEWAR ('Phil. Mag.,' (4) vol. 47, p. 334). The numbers given in brackets are those calculated by GRAHAM on the basis that the specific gravity of palladium wire is 12·38. In the last four experiments the palladium was charged electrolytically with hydrogen, and it follows directly from a consideration of the table that, no matter whether the palladium exists as black, sponge, foil, wire, or compact metal, or whether it is charged by exposure to hydrogen gas (the proper conditions being observed), or charged electrolytically, the amount of hydrogen occluded in each case is approximately the same.

If we wish to express, by means of a formula, the composition of palladium hydrogen, then, by choosing the nearest whole numbers, we arrive at the formula Pd_3H_2, which was first proposed by DEWAR (*loc. cit.*), and which corresponds with the ratio 1·5, instead of varying between 1·37 and 1·47, as above.

It must be observed, however, that in all cases in which the palladium has received the maximum charge of hydrogen the amount of hydrogen taken up is always in excess of that required for the formation of a definite chemical compound Pd_3H_2. If we admit—and this is not at all improbable—that such a compound is still capable of occluding or condensing hydrogen in the ordinary way, then the excess of hydrogen which is absorbed does not exclude the possibility of the formation of a definite compound of this composition. On the other hand, evidence in favour of its existence is of a very meagre kind, and is, we think, chiefly confined to the approximation of the ratio Pd/H to the theoretical value 1·5.

The views of chemists and physicists on the nature of palladium hydrogen have from time to time undergone considerable change. In 1869 GRAHAM ('Researches,' p. 290) wrote :—"The idea forces itself upon the mind that palladium, with its occluded hydrogen, is simply an alloy of this volatile metal (hydrogenium), in which

* Details will be found on p. 125.

the volatility of the one element is restrained by its union with the other, and which owes its metallic aspect equally to both constituents."

In 1874, however, another view was suggested by TROOST and HAUTEFEUILLE ('Ann. Chim. Phys.,' (5) vol. 2, p. 279). From experiments on the vapour pressure of palladium hydrogen at different temperatures, they conclude that the first addition of hydrogen to palladium forms a definite chemical compound Pd_2H, and that the excess of hydrogen over and above that required to form this compound is then occluded or absorbed in the usual way.

By subjecting the results of TROOST and HAUTEFEUILLE to a critical analysis, and from more extended experiments by himself and ROOSEBOOM, HOITSEMA ('Zeitschr. Physikal. Chem.,' vol. 17, p. 1, 1895) has arrived at an entirely different conclusion, namely, that, as regards the vapour pressure experiments, there is no decisive evidence for the formation of a definite chemical compound; and he further suggests that the results are in better agreement with the view that two immiscible solid solutions are formed. This appears to resolve itself into the formation of two alloys instead of one, as suggested by GRAHAM.

In confirmation of the arguments of HOITSEMA against the supposed formation of a compound having the formula Pd_2H, we have also the fact, first observed by FAVRE ('Comptes Rend.,' vol. 77, p. 649, and vol. 78, p. 1257) and confirmed by ourselves, that the heat of occlusion of hydrogen by palladium remains constant throughout the whole range of absorption.

If a chemical compound Pd_2H were first formed, we should expect to get a certain definite evolution of heat per gram of hydrogen combined for the hydrogen first admitted, and then, after sufficient hydrogen had been added to form the compound Pd_2H (about 630 volumes), we should expect to find a different value for the heat evolved per gram of hydrogen occluded or dissolved or absorbed. We have, therefore, confidence in discrediting the supposed formation of Pd_2H.

It would seem that HOITSEMA's conclusions apply equally well to the supposed formation of Pd_3H_2. But before finally dismissing the possibility of its existence we consider that some additional evidence is desirable. It is proposed to attack the problem from another and independent point of view, and it is hoped that all doubts, which are liable to affect any process in which it is uncertain whether equilibrium has really set in or not, will be overcome.

IX. *On the Heat of Occlusion and the Heat of Condensation.*

It has sometimes been suggested (*cf.* FAVRE, 'Ann. Chim. Phys.,' (5) vol. 1, p. 209), that the heat of occlusion of a gas represents the heat of condensation or liquefaction of the gas in the capillary pores of the absorbing substance. Now if this is so, and we vary the absorbing substance, at the same time maintaining it always at the same temperature, say 0° C., so that its specific heat shall play no part in the reaction, then it would seem justifiable to suppose that in the liquefaction of one gram of one and the same gas, hydrogen for example, in different absorbing substances, the *same* amount of heat, viz., the heat of condensation of one gram of hydrogen, would always be evolved.

We have found, for the heat of occlusion of one gram of hydrogen in platinum and palladium, the following values :—

Platinum	+ 68·8 − 2·7 = 66·1 K. per gram.
Palladium	+ 46·4 − 2·7 = 43·7 K. ,,

In order to obtain the difference between the initial and final values of the internal energy of the system, we require to subtract the heat equivalent of the work done by the atmosphere. For one gram molecule of a gas this amounts to 0·02 T.K. (2 T. g. cal.), and hence for half a gram molecule of hydrogen at 0° C. we require to diminish the above values for the heat of occlusion by 2·7 K. Since the numbers which we thus obtain are by no means approximately equal, we are of opinion that the phenomenon of the occlusion of hydrogen by platinum and palladium black is not simply the liquefaction or condensation of the gas in the capillary pores of the metals.

The same arguments would, doubtless, be valid in a comparison of the heat of occlusion with the heat of solidification or fusion.

X. *The Influence of Increased Pressure on the Occlusion of Hydrogen by Palladium Black.*

We have already seen that the composition of palladium hydrogen, fully charged with hydrogen at ordinary atmospheric pressure, corresponds approximately to the formula Pd_3H_2. Although from the experiments of HOITSEMA and ROOSEBOOM it would seem that increase of pressure should produce little or no effect on the occlusion of hydrogen by palladium, an experimental demonstration was deemed desirable. The details of the experiment were the same as in the corresponding experiment with platinum black ('Phil. Trans.,' A, 1895, vol. 186, p. 675). A quantity of palladium black was charged with hydrogen and shut up with an excess of hydrogen in the shorter graduated limb of a glass U-tube. After equilibrium had been established, the volume, temperature, and pressure of the enclosed gas were noted. Successive quantities of mercury were then poured into the longer limb, and the measurements repeated.

The results are contained in the following table :—

Palladium black used, 0·878 gram.

Volume of enclosed gas.	Temperature.	Pressure (millims. Hg. at 0° C.).	PV.	Volume reduced to 0° C. and 760 millims.
cub. centims.				cub. centims.
128·1	19°·14	810	103,800	127·6
74·8	19·14	1380	103,200	126·9
48·0	19·14	2151	103,300	127·0
36·5	19·14	2821	103,000	126·6
29·5	19·14	3496	103,100	126·8

The fact that the volume energy (PV), or the reduced volume of the gas, except for the first increment of pressure, may be taken as constant, satisfactorily establishes the conclusion that increase of pressure, at least up to 4·6 atmospheres, practically has no effect on the occlusion of hydrogen by palladium black which has already absorbed the maximum quantity of hydrogen at the ordinary temperature. Platinum and palladium black thus behave in precisely the same way as regards the effect of pressure on the occlusion of hydrogen. The first increase of pressure caused the disappearance of several volumes (about ten volumes) of hydrogen, but as this does not continue, it may possibly be due to the presence of moisture, derived from the palladium black, in the gas.

The influence of pressure on the occlusion of hydrogen by palladium at high temperatures has recently been described by DEWAR ('Proc. Chem. Soc.,' 1897, No. 183, p. 192).

XI. *The Heat of Absorption of Oxygen by Palladium Black.*

It is fairly certain that, on the absorption of oxygen by palladium black, a definite oxide, or a mixture of definite oxides, is formed. A redetermination of the heats of formation of the different oxides of palladium is outside the scope of this inquiry, but it seemed desirable to determine the heat of absorption of the oxygen actually contained in palladium black, for the purpose of comparing the number so found with the corresponding number for platinum black. Since it was impossible to make the measurement directly, an indirect method was employed, viz., the estimation of the amount of heat *absorbed* on the *removal* of the oxygen from palladium black.

A quantity of palladium black was introduced into the calorimeter, and fully charged with hydrogen. A portion of the hydrogen absorbed was thus really occluded, whilst the remainder removed the oxygen contained in the palladium black as water. After the heat change had been measured, the occluded fraction was easily ascertained by exhausting at a red heat, and from this the volume of oxygen removed from the palladium black was found.

Assuming, as was necessary in the case of the corresponding experiment on platinum black (*q.v.*, 'Phil. Trans.,' A, 1897, vol. 190, p. 149), that no appreciable heat change is involved in the mere wetting of the palladium by the water formed, and knowing the total heat of the reaction, the heat of formation of water, the heat of occlusion of the hydrogen, and the quantity of oxygen removed, we can calculate the heat absorbed on its removal.

The results obtained in three independent experiments are given below in tabular form. The amounts of hydrogen occluded and oxygen removed are expressed in cubic centimetres, volumes (Pd. bk. = 1), and grams; and it will be seen that there is a very satisfactory agreement among themselves of the values representing the number of volumes of hydrogen occluded and the number of volumes of oxygen removed.

CALORIMETRIC Experiments on the Absorption of Oxygen by Palladium Black.

		I.	II.	III.
Palladium black used	Grams	0·4789	1·0237	1·0570
" " "	Cub. centims.	0·0399	0·0853	0·0881
Hydrogen occluded	Cub. centims.	34·32	74·08	76·51
" "	Volumes	860	868	868
" "	Grams	0·003089	0·006667	0·006886
Hydrogen burnt to water	Cub. centims.	11·19	24·02	25·16
" " "	Grams	0·001007	0·002162	0·002264
Oxygen removed	Cub. centims.	5·595	12·01	12·58
" "	Volumes	140	141	143
" "	Grams	0·008000	0·01717	0·01799
Heat due to formation of water (calculated)	K.	0·3444	0·7394	0·7743
Heat due to occlusion of hydrogen (calculated)	K.	0·1433	0·3093	0·3195
Sum of last two	K.	0·4877	1·0487	1·0938
Heat evolved, corresponding to the deflection	K.	0·3927	0·8424	0·8931
	Millims.	373·0	800·0	848·1
Difference = heat absorbed on the removal of the oxygen	K.	0·0950	0·2063	0·2007
Heat absorbed per gram of oxygen removed	K.	11·9	12·0	11·2

The three values of the heat *absorbed* per gram of oxygen *removed*, or, what amounts to the same thing, the heat evolved per gram of oxygen absorbed, are thus + 11·9, + 12·0, and + 11·2 K., whilst the mean of the three is + 11·7 K. This number, referred to 16 grams of oxygen, becomes + 187 K. (+18700 gram calories).

From the nature of these experiments it is difficult to say within what limits of error this number may be taken as correctly representing the heat of absorption of oxygen in palladium black. As far as such measurements go, however, the agreement between the individual numbers may be said to be satisfactory.

Whilst the heat of occlusion of hydrogen in palladium is less than the corresponding number for platinum, the heat of absorption of oxygen is slightly greater. It will be remembered that the heat of absorption of oxygen in platinum black, viz., + 176 K. per gram atom, is almost identical with the number given by JULIUS THOMSEN for the heat of formation of platinous hydroxide, $Pt(OH)_2$, viz., + 179 K., thereby furnishing presumptive evidence that the absorption of oxygen by platinum black is a true oxidation phenomenon, the water necessary for the formation of the hydroxide being always present in platinum black.

It therefore remains to be seen whether there is any sort of agreement between the numbers representing the heat of absorption of oxygen by palladium black and the heat of formation of an oxide or hydroxide of palladium.

JOANNIS ('Comptes Rend.,' vol. 95, p. 295) determined the heat of formation of palladous hydroxide, $Pd(OH)_2$ (oxide ?), by precipitating the substance from a solution of (1) potassium palladobromide, (2) potassium palladochloride, by means of caustic potash, and obtained the values + 193·4 K. and + 208·8 K., the mean of the two being about + 200 K.

JULIUS THOMSEN ('Thermochem. Untersuch.,' vol. 3, p. 436) also determined the same heat of formation by precipitating a solution of sodium palladochloride by caustic soda, and gives as its value + 227 K., thus :—

$$\mathbf{Pd} + O + H_2O = \mathbf{Pd(OH)_2} + 227 \text{ K.}$$

There is thus a discrepancy of about 27 K. between the results obtained by the two observers.

The heat of formation of palladic hydroxide was also determined by THOMSEN in a similar way, with the following result :—

$$\mathbf{Pd} + 2O + 2H_2O = \mathbf{Pd(OH)_4} + 304 \text{ K.}$$

This number refers to 32 grams of oxygen; for 16 grams it therefore becomes + 152 K.

The value found by us for the heat of absorption of oxygen in palladium black lies intermediate between the values given by THOMSEN for the heats of formation of palladous and palladic hydroxide, and, considering the difference between the numbers representing the heat of formation of the lower compound as determined by THOMSEN and JOANNIS, the heat of absorption of oxygen in presence of sufficient moisture may be consistent with the formation of either the higher or lower hydroxide, or possibly with a mixture of both. In any case, it is of the same order of magnitude, and taken in conjunction with the behaviour of palladium black when heated in an atmosphere of oxygen, is undoubtedly in harmony with the view that the absorption of oxygen by palladium black is a true phenomenon of oxidation.