On the Occlusion of Oxygen and Hydrogen by Platinum Black. Part II

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VI. *On the Occlusion of Oxygen and Hydrogen by Platinum Black.*—Part II.

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CONTENTS.

I. *Introduction.*

IN a former paper ('Phil. Trans.,' A, 1895, vol. 186, p. 657–693) we gave an account of some experiments on the occlusion of oxygen and hydrogen by platinum black, and pointed out that freshly-made platinum black invariably contains a considerable quantity of oxygen. Most of the specimens which we examined contained approximately 100 volumes, or 0·66 per cent. of oxygen, which could only be completely removed by heating *in vacuo* at a dull red heat, and although a large fraction of the total oxygen can be extracted at about 400° C., the substance which remains behind is no longer platinum black but platinum sponge which has a much lower absorptive power for gases.

When hydrogen is admitted to platinum black containing x volumes of oxygen, $2x$ volumes are converted into water, and the remainder of the gas absorbed, which, in general, is about 100 volumes, is really occluded. The heat evolved on the occlusion of hydrogen by platinum black has been measured by BERTHELOT ('Ann. de Chim. et de Phys.,' 1883, vol. 30, p. 519), and by FAVRE ('Comptes Rend.,' vol. 77, p. 649, and vol. 78, p. 1257), but we have already (*loc. cit.*, p. 693) expressed ourselves as dissatisfied with the results they obtained, since the heat due to the combination of the oxygen pre-existing in the platinum black with the hydrogen is also included in these measurements.

During our attempts to solve the problem whether the occlusion of gases by metals is a chemical or physical phenomenon, we have investigated the thermal changes which take place on the occlusion of hydrogen and oxygen by platinum black. Independent of the object for which the investigation was undertaken, the results we have obtained, which we now beg to lay before the Society, are of interest in connection with many electrical experiments where platinum or platinised electrodes are employed. The present communication also contains an account of the behaviour of several other gases towards platinum black, together with some speculations regarding the occlusion of oxygen.

II. *The Heat of Occlusion of Hydrogen by Platinum Black.*

In attempting to determine the heat evolved on the occlusion of hydrogen by platinum black several courses were open to us. The first of these, namely, the preparation of pure platinum black, and the subsequent treatment of this with hydrogen in the calorimeter, had to be abandoned, as we have up to the present been unable to obtain this substance free from occluded gases.

A second conceivable method would be to treat platinum black as we find it, that is to say, platinum black containing oxygen, small quantities of carbon dioxide, and usually traces of other substances,* with hydrogen, and to make a correction for the heat evolved due to the formation of water. This method, however, has two disadvantages; firstly, the correction for the heat evolved on the formation of water is much greater than the constant to be measured, and secondly, it is very difficult to estimate exactly the quantity of oxygen in the sample experimented upon. Any attempts to remove the oxygen by heating *in vacuo* resulted in the formation of platinum sponge, which occludes relatively only small quantities of hydrogen.

As will be seen in Section III., chemical methods for removing the oxygen without introducing other deleterious substances also proved unsuccessful, and hence we were reduced to the third alternative. This consisted in fully charging up the platinum black with hydrogen at atmospheric pressure, removing as much as possible of the hydrogen by means of the pump, at as high a temperature as the platinum black could safely stand (184° C.) without being converted into sponge, and finally charging up fully again with hydrogen in the calorimeter. In this way the hydrogen converts all the oxygen initially present in the platinum black into water (the bulk of which is subsequently removed), and also exerts its full influence on oxides of nitrogen or other impurities before the heat evolved on the true occlusion of hydrogen is measured in the calorimeter.

It seems to us that the only objection which can be raised to this method of

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* The chief of these are oxides of nitrogen, derived from nitroso compounds formed on the solution of platinum in *aqua regia*, and which cannot be destroyed even on repeatedly evaporating the solution successively with water and hydrochloric acid.

determining the heat of occlusion is in connexion with a statement of BERTHELOT'S,[*] that two definite compounds of platinum and hydrogen exist, viz., $Pt_{30}H_2$ and $Pt_{30}H_3$, corresponding to the amount of hydrogen which can be extracted from platinum black *in vacuo* at two different temperatures and to two different heats of occlusion. FAVRE,[†] also, found on admitting hydrogen fractionally, in small portions at a time, that the heat evolved per gram of hydrogen occluded became less and less. As our results will show, the heat evolved per gram of hydrogen occluded for the fraction of hydrogen which can be removed at the ordinary temperature, by means of the pump, from platinum fully charged with hydrogen at atmospheric pressure, is the same as for the portion which can be extracted *in vacuo* at 184° C., and consequently we believe that the results obtained by BERTHELOT and by FAVRE were due to the fact that the samples of platinum black examined by them contained oxygen.

Having stated in general terms the method adopted by us for the determination of the heat of occlusion of hydrogen by platinum black, we will now describe the apparatus employed.

During the first part of this investigation we found that although the bulk of the hydrogen or oxygen occluded by platinum black was absorbed almost immediately, a slow absorption went on for hours. This being the case, we found it better to make use of a Bunsen's ice calorimeter instead of an ordinary water calorimeter, which gives the best results when the reaction is nearly instantaneous. We are of opinion that the ice calorimeter has been too often neglected on account of the difficulty of obtaining pure snow; but, by adopting the device suggested by Professor C. V. BOYS,[‡] we have been able to obtain very satisfactory results. The calorimeter itself, L, which was made sufficiently large to accommodate the experimental tube D, was surrounded by an air-jacket, J, as shown in fig. 1, and the whole suspended inside three concentric cylinders. The cylinders themselves, with their drain-pipes, were sunk in a large cubical wooden box, the space between the outer cylinder and the box being packed with cotton wool. Pounded Norwegian ice was placed inside the cylinders and heaped up outside, so that the whole of the projecting part of the experimental tube was covered with melting ice. The function of the air-jacket is to diminish the too rapid transference of heat between the calorimeter, which should be exactly at 0° C., and the melting ice, which, since it is more or less impure, has always a lower melting-point than pure ice. The calorimeter was filled in the usual way with boiled-out distilled water, and, after some mercury had been introduced into the lower part, the thistle funnel, tap, and side capillary tube were sealed on. In order to produce the sheath of ice on the outside of the inner tube of the calorimeter, the whole was cooled down to 0° C., and some solid carbon dioxide introduced. This produced intense local undercooling, and consequently some ice crystals

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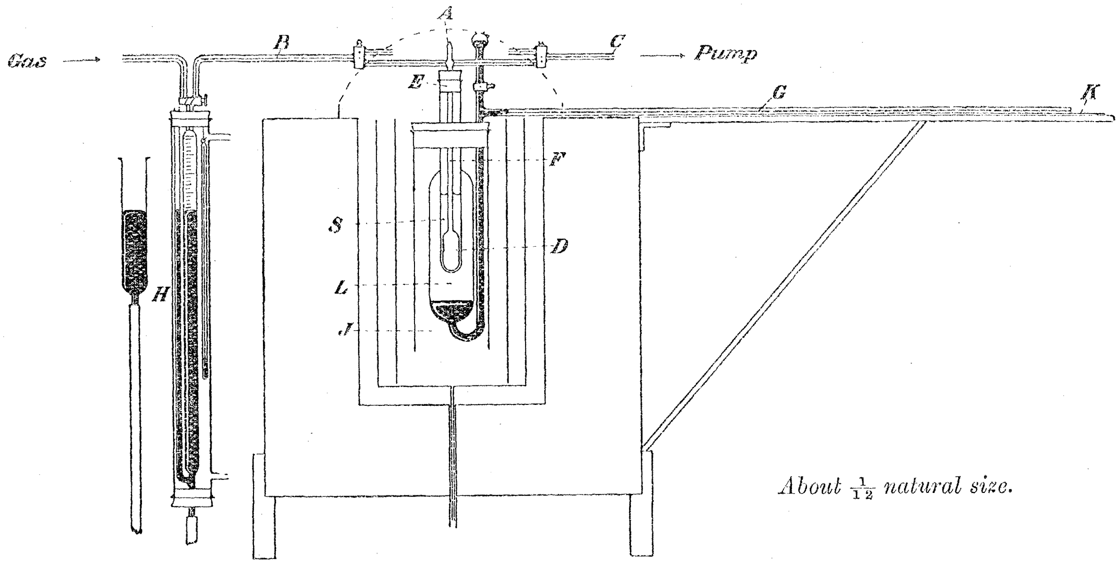
[*] BERTHELOT, *loc. cit.*

[†] FAVRE, *loc. cit.*

[‡] C. V. BOYS, 'Phil. Mag.,' 1887, vol. 24, p. 214.

separated out.[*] The ice sheath was then made to grow to the required size by pouring ether into the inner tube and blowing a current of air through it. Lastly, sufficient salt solution, S, cooled down to zero, was introduced into the inner tube, so that when the experimental tube was inserted, the whole of the bulb and a considerable portion of the stem were covered with the solution; and care was also taken that the surface of the salt solution was 3 or 4 centims. below the top of the ice-sheath, so that most of the heat radiating from it would be caught in the sheath. The amount of mercury sucked into or expelled from the apparatus was preferably determined by the deflection of the meniscus in the capillary tube, rather than by weighing, since the progress of the reaction could easily be seen at any instant. No errors due to the "sticktion" of the mercury need be feared if the tube is tapped occasionally. The capillary tube was one especially selected from a large number. For over a metre of its length its mean capacity was 0·0001196 cub. centim. per millim., and the deviations from the mean value at ten points along its length were respectively + 9, + 17, + 6, − 1, + 4, − 11, − 16, − 1, + 1, − 7, units in the last significant figure. In translating the deflection of the mercury meniscus in millims. into heat units, we have accepted DIETERICI's[†] value, that 1 gram calorie corresponds to the displacement of 0·01544 gram of mercury; and hence a deflection of 1 millim. in the tube we employed represents 0·1053 of a gram calorie, or 0·001053 of a hundred-gram calorie, denoted by K in this paper.

Fig. 1.



About $\frac{1}{12}$ natural size.

Before proceeding to use the calorimeter for our experiments, the specific heats of

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[*] If this precaution is not taken, the water may be cooled several degrees below 0° C., and, when once ice begins to form, it does so so suddenly that the apparatus is liable to burst.

[†] DIETERICI, 'Wied. Ann.,' 1889, vol. 37, p. 499.

pure lead and zinc were determined, to see that everything was in good working order. The values we found were as follows:—

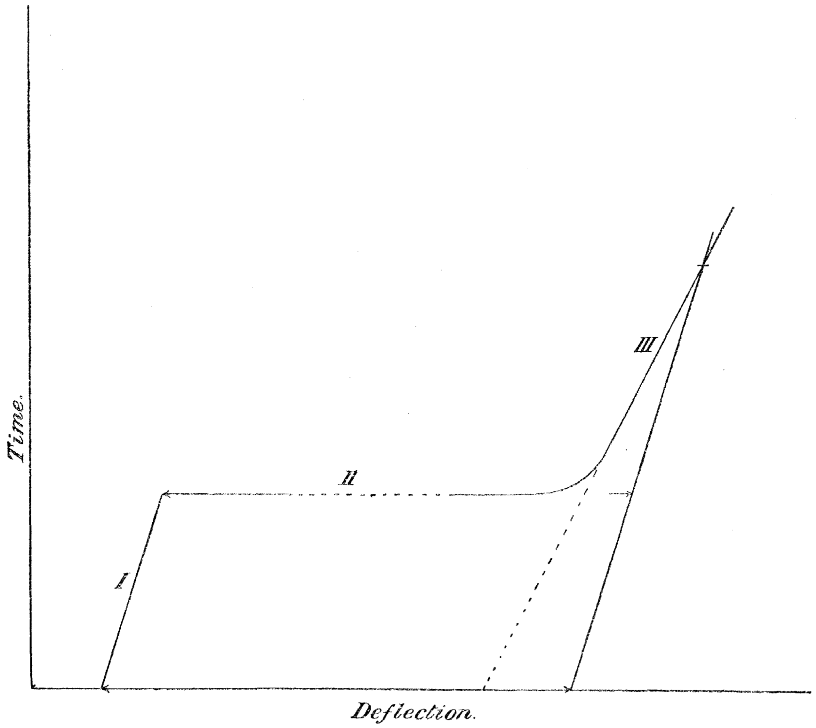
Specific heat of lead	*0·0299*	between	0°	and	38°0 C.
Spring found	0·0305	,,	17°	,,	108° ,,
	0·03195	,,	13°	,,	197° ,,
	0·03437	,,	16°	,,	292° ,,
Specific heat of zinc	*0·09312*	between	0°	and	15°·8 C.
Kopp found	0·0932	Temperature interval not stated.			
Bunsen found	0·0935				
Schüller and Wartha found	0·0939				

The numbers we find are lower than those recorded by other observers, but this, at least in the case of lead, is as it should be, since the determination was made at a lower temperature.

Having satisfied ourselves that the instrument gave correct results, an experimental tube of the form shown in fig. 1 was made. It consisted of a bulb, D, to contain the platinum black, which along with a portion of the stem was immersed in the salt solution contained in the inner tube of the calorimeter. Communication between the bulb and the system of taps and capillary tubes which projected above the calorimeter was made by means of a tube F, just sufficiently wide to admit of the introduction of the platinum black. When the experimental tube was in position, the mouth of the inner tube of the calorimeter was closed by the india-rubber stopper E. After a known weight of platinum black had been introduced, and before the apparatus was finally fixed in position in the calorimeter, the tube F was sealed off at the point A. The tube B was now connected with a gas burette whilst C was placed in communication with the pump, and the capacity of the tube determined by filling with dry air at a known temperature and pressure, exhausting and remeasuring at the same temperature and pressure.

The platinum black was now fully charged up by admitting pure hydrogen under atmospheric pressure. After standing for a day, the tube was jacketed with aniline vapour at 184°, and the excess of hydrogen filling the apparatus, together with the hydrogen and water which can be removed *in vacuo* at the ordinary temperature, and that which is given off at 184° C., extracted by means of the pump. Both taps being now shut, the experimental tube in a vacuous state was cut off, cooled to 0°, and introduced into the calorimeter. In this position it was again connected up with the hydrogen apparatus and the pump, and when equilibrium had set in, hydrogen was admitted, from a gas burette, and the deflection of the mercury meniscus in the capillary side tube, G, noted from time to time until equilibrium was presumably again established. As a rule the position of the meniscus in the capillary tube never remains stationary, whether an experiment is in progress or not, in consequence of the very slow melting of ice or freezing of water inside the calorimeter. When the ice is first produced in the calorimeter the whole apparatus must stand for several days surrounded by ice before equilibrium between the ice and water inside is established. Owing to adventitious circumstances, atmospheric pressure, etc., the normal creepage of the meniscus sometimes amounted to several millims. an hour, but experiments were never conducted until this had diminished to one or two millims., whilst in most of the experiments the normal creepage was less than one millim. per hour.

Fig. 2.



After admitting hydrogen the normal creepage was never the same, as, even after three or four hours, hydrogen continues to be slowly absorbed. This difficulty was overcome in the following way:—After the last reading of the deflection was taken, the volume of hydrogen used was immediately noted, and by subtracting what was required to fill the experimental tube at 0° C. (the top of the tube and the taps being covered with melting ice) the quantity of hydrogen occluded up to the time of the last reading of the deflection was found. The final occlusion of hydrogen was of course very slow, and the real calorimeter deflection was obtained by plotting the readings in a co-ordinate system as shown in fig. 2.

The first part of the curve I, represents the normal creepage before the admission of hydrogen. The horizontal part II, a large portion of which is omitted, shows the chief deflection due to the main occlusion of the hydrogen during the first few minutes (10–15 min.). The curve then bends upwards, III, but never becomes quite parallel with the first part owing to the very slow absorption going on. Instead of drawing the tangent to part III. of the curve, which would obviously be wrong, a closer approximation to the true deflection can be obtained by drawing a parallel to part I. of the curve through the last point of observation, at which point the volume of occluded hydrogen was determined.

Blank experiments showed that admission of the relatively small quantity of gas from the burette to an empty experimental tube produced no appreciable deflection.

Several preliminary experiments were made, using small quantities of platinum black, but the results of these were unsatisfactory on account of the difficulty of measuring the deflection and the amount of hydrogen occluded accurately enough. To obviate this difficulty, experiments were made on a larger scale, and with as much platinum black as could conveniently be introduced into the experimental tube. The results of these experiments are given in the following Table I., the experimental tube being removed from the calorimeter, re-exhausted at 184° C., and replaced in the calorimeter again before admitting hydrogen the second time.

TABLE I.

Experiment.	Platinum black used.	Hydrogen occluded.		Heat evolved.		Heat evolved per gram of hydrogen occluded.
				Deflection.	Heat in calories. 1 K = 100 cal.	
	grams.	cub. centims.	grams.	millims.	K.	K.
I.	9·744	8·34	0·000751	49·6	0·05223	69·6
II.	9·744	7·38	0·000664	43·6	0·04591	69·1

TABLE II.

Experiment.	Platinum black used.	Hydrogen occluded.		Heat evolved.		Heat evolved per gram of hydrogen occluded.
				Deflection.	Heat in calories. 1 K = 100 cal.	
	grams.	cub. centims.	grams.	millims.	K.	K.
I*a*.	9·744	−2·51	−0·000226	−14·1	−0·01485	−65·7*
I*b*.	9·744	2·13	0·000192	11·6	0·01221	63·7
III.	1·9193	1·90	0·000171	11·1	0·01169	68·3

The mean of the two results is an evolution of 69·4 K per gram of hydrogen occluded. This value, however, may represent the sum of two other values, one of which relates to the heat evolved on the occlusion of the hydrogen, which can be

* Heat *absorbed* per gram of hydrogen *removed*.

extracted from fully charged platinum black *in vacuo* at the ordinary temperature, whilst the other corresponds to the occlusion of the hydrogen, which can be removed from the platinum black *in vacuo* by raising its temperature from the ordinary temperature up to 184° C. In order to test the question whether the occlusion of different fractions of hydrogen corresponds to different heat changes, as has been stated by FAVRE and BERTHELOT, some additional experiments were made, the results of which are given in tabular form in Table II.

When Experiment I. was over, the platinum black remained fully charged with hydrogen at 0° C. Before removing the experimental tube from the calorimeter for the purpose of re-exhausting it at 184°, an attempt was made to measure the heat *absorbed* on removing as much of the hydrogen as could be pumped off at 0° C., with the results given under Experiment I*a*. As will be seen from the table, 2·51 cub. centims. of hydrogen were removed. In Experiment I*b*. the platinum black was again fully charged up with hydrogen. The results of these two experiments, namely, 65·7 K *absorbed* per gram of hydrogen *removed*, and 63·7 K evolved per gram of hydrogen occluded, are sufficiently close to each other and to the mean value 69·4 K, considering the probable errors which will be discussed immediately, to show that there is no difference between the thermal changes which take place when the two different fractions of hydrogen are occluded. In Experiment III. a small quantity of platinum black was employed, and it was exhausted at 230° C. instead of at 184° C. before being placed in the calorimeter. Approximately, the same value was obtained for the heat evolved per gram of hydrogen occluded.

The probable accuracy of the results may be estimated from the following considerations. The hydrogen was measured in a calibrated burette, H, divided into tenths of a cubic centimetre, which was read to one-hundredths of a cubic centimetre. The volume of hydrogen occluded (always reduced to 0° C. and 760 millims.), given in the foregoing tables, represents the difference between the total hydrogen measured and that required to fill the experimental tube. The measurements are also liable to slight errors involved in reading temperature and pressure for the reduction of the gas volumes to standard conditions. The burette could be read with certainty to one-fiftieth of a cub. centim., but if we allow the error from all sources to be one-twentieth of a cub. centim., this would mean in Experiments I. and II. a possible error of about $\frac{3}{4}$ per cent.; whilst in I*a*., I*b*., and III. the error might amount to $2\frac{1}{2}$ per cent. The calorimeter deflection, which was observed on a scale etched on a plate-glass mirror, K, lying underneath the capillary tube, could be read accurately to 0·1 of a millim.; but, if we admit a total error of 0·5 of a millim. for plotting the curve and for any change of normal creepage during the experiment, then the error involved in the heat measurement may approach 1 per cent. in Experiments I. and II., and 5 per cent. in Experiments I*a*., I*b*., and III.

The total error in the most unfavourable circumstances in the first two experiments may thus amount to about one and a half per cent., whilst in the last three it might exceed seven per cent.

If we take the mean of Experiments I., II., and III., and also include another independent result, 68·2 K, which was obtained incidentally during the determination of the heat evolved on the occlusion of oxygen by platinum black,[*] we find as the general mean value for the heat evolved per gram of hydrogen occluded, 68·8 K, or 137·6 K per gram-molecule; and we think that, with the liberal allowances we have made for experimental error, this number may be taken as correct within one or two per cent.

According to BERTHELOT the hydrogen which cannot be pumped off at the ordinary temperature from platinum black charged with hydrogen forms the compound $Pt_{30}H_2$, whilst that which does come off is obtained by the dissociation of $Pt_{30}H_3$ into the first compound and hydrogen.

The heats of formation of these hypothetical compounds are + 339 K for the first, and + 426 K for the second; that is to say, + 170 K are evolved per gram of hydrogen occluded in the first instance, and 87 K per gram in the second. From the results which we have obtained it follows that the arguments put forward by BERTHELOT in favour of the existence of these compounds cannot be justified. The second value for the heat of occlusion of hydrogen, which is only half the first, is still much higher than the real value, 68·8 K, and we can only account for these different and high numbers found by BERTHELOT on the assumption that the platinum black employed by him contained oxygen. If reference is made to Table III.[†] it will be found that when the platinum black contained oxygen, the following numbers were found by us for the heat evolved per gram of hydrogen *absorbed:* 203, 195, 183, 173, and 163 K, which are of the same order of magnitude as that given by BERTHELOT for the supposed heat of occlusion of hydrogen in the first compound, viz., 170 K.

FAVRE has attempted to distinguish between the heats evolved on the occlusion of hydrogen by platinum and by palladium, inasmuch as when hydrogen is admitted in small portions at a time to palladium, the heat of occlusion remains constant; whilst in the case of platinum the heat evolved becomes gradually less and less. This difference, which however is only apparent, is also exemplified in Table III., and it is only necessary to point out that it is the result of adding hydrogen to platinum charged with oxygen, and therefore, in this respect, the supposed difference between the behaviour of platinum and palladium to hydrogen does not exist.

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[*] Page 145, Table III, Operation 15.

[†] Page 145.

III. *On some Attempts to remove the Oxygen from Platinum Black without destroying its Occlusive Power* (*Occlusion* SO_2, CO, NH_3, *&c.*).

As far as we know the thermal change which takes place when oxygen is occluded by platinum black has never been measured. In 1883 the attempts which BERTHELOT made in this direction proved fruitless. We have already pointed out that platinum black, as usually prepared, invariably contains oxygen which cannot be removed by heating *in vacuo* without destroying the black and converting it into sponge, and consequently we tried a large number of experiments, having for their ultimate object the removal of the oxygen from platinum black, or, in other words, the preparation of a sample which *per se* at 0° C. would occlude oxygen directly.

All our attempts to prepare such a specimen have hitherto been unsuccessful, but some of them which are interesting in themselves may be briefly recorded here.

Sulphur dioxide.—One of the first of these was to treat platinum black with sulphur dioxide, in the hope that the sulphur trioxide formed, along with any occluded sulphur dioxide, might be completely extracted *in vacuo* at a temperature which would not impair the absorptive power of the platinum black for oxygen.

It was found, however, that although practically all the oxygen was removed as SO_3 in this way, the platinum black itself was charged with 84·2 volumes of sulphur dioxide. Of this occluded sulphur dioxide, which for the purpose we had in view was quite as objectionable as oxygen, only about one-fifth, or 15 volumes, could be removed *in vacuo* at the ordinary temperature; whilst for its complete removal ignition at a red heat, and consequently the conversion of the black into sponge, was necessary.

From the fact that the platinum black originally contained about 79·5 volumes of oxygen, and that 84·2 volumes of SO_2 were subsequently occluded, it may be inferred that platinum black occludes approximately the same number of volumes of both gases.

Carbon monoxide.—As we already know from former experiments, carbon dioxide may be readily removed from platinum black at temperatures which do not seriously affect its absorptive power. Attempts were therefore made to convert the oxygen contained in platinum black into carbon dioxide by the admission of carbon monoxide. Experiments showed that the bulk of the oxygen could be easily removed in this way, but on exhausting the tube it was found that carbon monoxide was itself occluded by the platinum black, and could only be removed by heating to redness in a vacuum.

In two experiments a sample of platinum black which contained initially about 90 volumes of oxygen was found to have occluded 95·7 and 93·5 volumes respectively of carbon monoxide.

Formic acid.—The method we have generally adopted for the preparation of platinum black has been by the reduction of sodium platinichloride by sodium formate, and it might be expected that the oxygen contained in platinum black could be removed by treatment with formic acid.

In the first of two experiments which were performed, the details of which need not be given, the platinum black was treated with the vapour of formic acid; whilst in the second, it was warmed with a dilute solution of formic acid in the experimental tube. In the latter case the excess of water and formic acid was evaporated off *in vacuo*, suitable absorbing agents having been introduced between the pump and experimental tube, and the residual substance dried at 100° C. *in vacuo* before exhausting at a higher temperature.

On gradually heating the platinum black obtained after treatment with (A), the vapour of formic acid, and (B), an aqueous solution of formic acid, gas was continuously given off *in vacuo* until a dull red heat had been maintained for some time. In both cases the gas pumped off was found to be a mixture of carbon monoxide and hydrogen, as shown in the following table.

	A. Platinum black treated with the vapour of formic acid.	B. Platinum black treated with dilute aqueous formic acid.
	vols.	vols.
CO	88·3	86·8
H_2	27·5	38·4
Total.	115·8	125·2

Hitherto we were inclined to ascribe the presence of oxygen in platinum black to the fact that it was washed and dried at 100° in the presence of air, since platinum black, when heated in an atmosphere of oxygen, absorbs this gas until the temperature reaches 360°–380° C. If freshly reduced platinum black contains either or both of these gases occluded in it, then it is easy to account for the presence of oxygen in the substance we actually obtain; for, on coming into contact with the air, both of these substances would be immediately burnt out and oxygen would take their place.

As a last resource for the preparation of pure platinum black, free from oxygen, we originally intended, if all else failed, to attempt to wash and dry it out of contact with the air; but these experiments show that even if we did succeed in keeping out oxygen, we might, it is true, obtain platinum black free from oxygen, but it would on the other hand be equally valueless for our purpose, since it would in all probability contain carbon monoxide and hydrogen.

Methyl alcohol, ammonia, &c.—Platinum black submitted to the action of the vapour of methyl alcohol, and then subjected to a preliminary exhaustion at 100° C., was found on heating to a red heat *in vacuo* to give off 101 volumes of a gas consisting of 11 volumes of carbon dioxide and 90 volumes not absorbed by alkaline pyrogallate. On transferring the latter to the eudiometer and exploding with oxygen, it was found to be composed chiefly of hydrogen, together with a small quantity of some hydrocarbon which was not further investigated.

On several occasions we have obtained specimens of platinum black of low absorptive power, which may readily be distinguished by the fact that they have a grey appearance instead of the usual dead black. (Platinum black of this description is apparently formed by the reduction of solutions which are acid instead of neutral or slightly alkaline.)

A quantity of this greyish platinum black from a preparation which on ignition in a vacuum gave off only 21 volumes of oxygen was treated with ammonia gas.*

After exhausting at the ordinary temperature, 24·8 volumes of gas were extracted on ignition and were found to consist of CO_2 4·2 volumes, O_2 0·0 volumes, H_2 15·6 volumes, and N_2 5·0 volumes.

The total gas extracted, viz., 24·8 volumes, is sufficiently close to 21 volumes, the amount of oxygen originally contained in another sample of the same preparation, to warrant the inference previously drawn with regard to sulphur dioxide, and confirmed in the case of carbon monoxide, hydrogen, methyl alcohol and formic acid, that, when these reducing substances act on platinum black the oxygen is removed but its place is taken by nearly the same number of volumes of the reducing substance or its products of decomposition. In former experiments, this number always approximated to 100 volumes, since the platinum black investigated contained nearly 100 volumes of oxygen. Furthermore, the removal of the reducing substance or its products from the platinum black seems to be just as difficult to accomplish as the removal of the oxygen itself.

An attempt to remove the oxygen by treating with hydrogen peroxide also proved unsuccessful.

When a platinum wire serves as the cathode in a vacuum tube through which an electric discharge is sent, the platinum volatilises, or gets thrown off, and forms a mirror on the walls of the tube. It was thought that by making a mass of platinum black the cathode in such a tube, the oxygen might be removed. On trying the experiment, however, only a very few bubbles of gas were extracted, and these were obviously due to the heating effect alone, and not to any mysterious action during the passage of the current.

In most of these experiments the reducing substance was employed in excess, but

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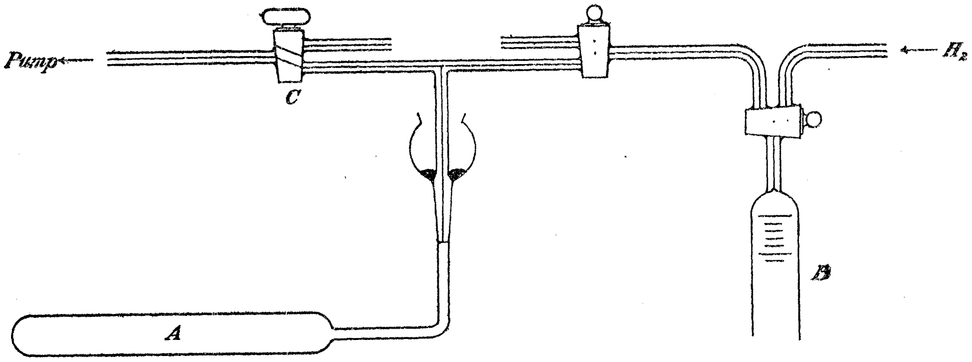
* The ammonia gas employed in this experiment was obtained by admitting strong aqueous ammonia at the bottom of a small flask, provided with a side tube dipping into mercury, nearly filled with chips of caustic potash, so that the gaseous ammonia given off might be dried as it ascended. When potash is dissolved in water, heat is evolved, and when ammonia is liberated from an aqueous solution, heat is absorbed, and the latter effect seems to be greater than the former, for, on admitting ammonia, the flask became very cold, and it was only necessary to warm it gently with the hand to obtain a steady stream of the gas.

in the following section the result of admitting the theoretical quantity of a reducing agent, viz., hydrogen, is described.

IV. *On the Existence of Platinum Oxygen and Platinum Hydrogen in presence of each other.*

All previous attempts to prepare a specimen of platinum black which would occlude oxygen directly having failed, the following experiments were made in the hope of obtaining the substance we were in search of. The amount of oxygen contained in a certain sample of platinum black was determined by a direct experiment; and it was found that 5·815 grams gave, on exhaustion *in vacuo* at a red heat, 25·56 cub. centims. = 92·6 volumes of oxygen. By taking another weighed quantity of the same sample and charging it with rather less than the amount of hydrogen theoretically necessary for converting all the oxygen into water, it was expected that the platinum black would then be in a position (after pumping off the water formed at the ordinary temperature) to absorb oxygen directly in the calorimeter. For this purpose 5·051 grams of platinum black were placed in the experimental tube, A, (fig. 3) which was then exhausted. It was estimated that this quantity of platinum black contained 22·20 cub. centims. of oxygen, for the complete conversion of which into water 44·4 cub. centims. of hydrogen would be necessary.

Fig. 3.



As a matter of fact, only 39·05 cub. centims. of hydrogen were admitted from the gas burette, B. The apparatus was then allowed to stand for a few hours, when the tap, C, communicating with the pump was opened. Practically all the hydrogen admitted was found to be absorbed, for on putting the pump in action only about a quarter of a cub. centim. of gas was extracted. On surrounding the experimental tube, A, with a copper sheath and applying a Bunsen burner, 10·75 cub. centims. of gas were pumped off, which on examination was found to consist of:—

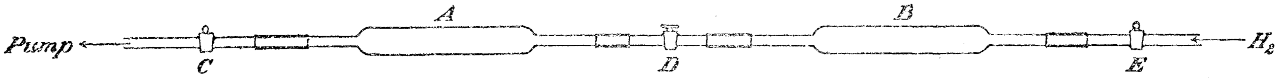
CO_2	2·53 cub. centims.	= 10·5 vols.
O_2	3·04 ,, ,,	= 12·7 ,,
H_2	5·00 ,, ,,	= 20·8 ,,
Residue	0·18 ,, ,,	= 0·7 ,,
Total	10·75 ,, ,,	= 44·7 ,,

It would appear, therefore, from this experiment that the hydrogen, on being admitted to the platinum black, attacks the portion with which it first comes in contact, converting the oxygen into water, and then takes its place, instead of first converting as much as possible of the oxygen into water. It is also noteworthy that the oxygen and hydrogen pumped off did not combine on passing over the heated platinum black or sponge, but this, perhaps, may be due to the fact that they come off at different temperatures, and that the bulk of the gas diffused at once into the Töpler pump, which had a much larger volume than the experimental tube. If this explanation is correct, then, even on allowing the tube to stand for weeks or months one could scarcely expect all the admitted hydrogen to combine with the oxygen in the platinum black, since the hydrogen is practically not given off into the vacuum again, and consequently could not diffuse along to the other end of the tube containing the occluded oxygen, and *vice versâ*.

That the explanation we have given is substantially correct was proved by slightly modifying the conditions of experiment.

5·330 grams of platinum black was divided into two portions of 2·608 grams and 2·722 grams, which were introduced into the hard-glass tubes, A and B respectively, of fig. 4.

Fig. 4.



The two portions were thus separated by a narrow tube provided with a stop-cock, D. When the whole apparatus, C A D B E, was exhausted, the stop-cock, C, was shut. It was calculated that 46·86 cub. centims. of hydrogen were sufficient to convert all the oxygen in both portions of the platinum black into water. 48·00 cub. centims., or rather more than what was theoretically necessary, were admitted from a gas burette through the stop-cock, E. After standing for about two hours, the communication between the two tubes remaining open all the while, the tap, C, was opened, and it was found that the vacuum inside the apparatus was practically complete, or that all the hydrogen which had been admitted was absorbed.

The stop-cock, D, was now closed, and the tube, A, nearest the pump, heated to a dull red heat and exhausted. When the exhaustion was complete, D was opened, and, A still being kept hot, the tube B was similarly exhausted at a red heat, and the gas collected separately.

The composition of the gases obtained in this way is shown by the following analysis :—

	Gas from tube A, adjacent to pump.	Gas from tube B, adjacent to burette.
CO_2	1·91 cub. centims. = 15·5 vols.	1·14 cub. centims. = 8·8 vols.
O_2	2·94 ,, ,, = 23·7 ,,	0·00 ,, ,, = 0·0 ,,
H_2	0·40 ,, ,, = 3·2 ,,	7·36 ,, ,, = 56·6 ,,
Total . .	5·25 ,, ,, = 42·4 ,,	8·50 ,, ,, = 65·4 ,,

These results confirm our previous statement that when a limited quantity of hydrogen is admitted to platinum black containing oxygen, it simply removes the oxygen, as water, from that portion of the platinum black with which it first comes into contact, and then takes its place; for it will be seen from the above Table that the platinum black in the tube adjacent to the burette contained an excess of hydrogen associated with it, whilst the portion next the pump contained an excess of oxygen.

Precisely the same thing, but only in reversed order, takes place when oxygen is admitted to platinum black charged with hydrogen, as an experiment performed in the converse way clearly showed.

These results show that, in the case of the first experiment which led to their being performed, we may have a given quantity of platinum black containing both, what we may be permitted provisionally to call, *platinum oxygen* and *platinum hydrogen*, but they give us no trustworthy indication of how much of each is present; for, it is more than likely that on heating, some of the oxygen from the platinum oxygen combines with some of the hydrogen from the platinum hydrogen forming water; and that the free gases finally obtained are only the portions which from accidental circumstances escape the catalytic action of the platinum.

The quantities of platinum oxygen and platinum hydrogen existing in the same sample are thus probably greater than the above experiments seem to indicate.

V. *The Heat of Occlusion of Oxygen by Platinum Black.*

Having failed in the preparation of a sample of platinum black which would occlude oxygen directly at 0° C., and so enable us to determine directly the heat of occlusion of oxygen, our only alternative was to remove as much of the oxygen as possible by charging with hydrogen and then to make allowance for the heat due to the formation of water in subsequently charging with oxygen.

All the experiments made in the preceding section go to show that if a portion of the oxygen in platinum black be discharged by the addition of even considerably less than the theoretical quantity of hydrogen, the resulting substance still contains platinum oxygen and platinum hydrogen existing together, and that the quantity of hydrogen pumped off such a mixture at a red heat, *in vacuo*, even although relatively small, does not necessarily represent the actual amount of hydrogen existing in the mixture as platinum hydrogen, but only that fraction of it which escapes the catalytic action of the platinum or platinum oxygen.

In the experiments which follow an attempt was made to reduce the amount ot this hydrogen to as small an extent as possible. The apparatus used was precisely similar to that employed for the determination of the heat evolved on the occlusion of hydrogen. The amount of platinum black used was 12·555 grams, and after its introduction, the capacity of the experimental tube was carefully determined.

According to calculation the above quantity of platinum black contained 55·18 cub. centims. of oxygen, and this requires for its complete conversion into water about 110 cub. centims. of hydrogen. Before placing the apparatus in the calorimeter it was sealed on, on one side to the pump, and on the other to the burette supplying pure hydrogen. After completely exhausting, at the ordinary temperature, 96·40 cub. centims. of hydrogen were admitted and allowed to remain overnight. Next day communication was made with the pump, and whilst the platinum black was heated in boiling aniline (temp. 184° C.), as much water and gas as possible were pumped off. In this way 1·52 cub. centims. of hydrogen were extracted. The experimental tube, in the vacuous state, was then removed from the pump and burette and its contents thoroughly mixed up by prolonged shaking. After having been shaken at intervals for a day it was cooled to 0° C. and inserted into the calorimeter and sealed on once more to the pump and to the burette, furnishing pure oxygen.

It was hoped that by this treatment all the platinum hydrogen might be destroyed and that the specimen would be able to occlude oxygen directly. Oxygen was, therefore, admitted in small portions of about 5 cub. centims. at a time, and the results are given in tabular form in Table III. For the sake of convenience, all the results have been tabulated together, and have been further sub-divided into a series of eight experiments, or twenty-seven operations.

TABLE III.—Calorimetric Experiments on the Occlusion of Oxygen by Platinum Black.

Experiment.	Operation.	Gas.		Gas absorbed.		Calorimeter deflection.	Heat evolved. K = 100 gram. cal.	Heat evolved per gram of gas absorbed.
		Admitted.	Exhausted.					
		cub. centims.	cub. centims.	cub. centims.	grams.	millims.		K.
I.	1.	5·32 O_2	Nil	5·32 O_2	0·00761 O_2	135·8	0·1430	18·8
	2.	5·51 ,,	,,	5·51 ,,	0·00788 ,,	133·0	0·1401	17·8
	3.	4·37 ,,	,,	4·37 ,,	0·00625 ,,	108·6	0·1143	18·3
	4.	5·28 ,,	1·74	3·54 ,,	0·00506 ,,	76·1	0·0801	15·8
	5.	25·86 ,,	24·96	0·90 ,,	0·00129 ,,	12·2	0·0129	10·0
			Totals .	19·64 ,,	0·02809 ,,	..	0·4904	
II.	6.	47·59 H_2	Nil	47·59 H_2	0·00428 H_2	826·8	0·8698	203·1*
III.	7.	5·03 O_2	Nil.	5·03 O_2	0·00720 O_2	151·2	0·1592	22·1
	8.	5·49 ,,	,,	5·49 ,,	0·00785 ,,	159·3	0·1678	21·4
	9.	5·08 ,,	,,	5·08 ,,	0·00727 ,,	148·3	0·1561	21·5
	10.	32·49 ,,	24·85	7·64 ,,	0·01092 ,,	149·1	0·1570	14·4
			Totals .	23·24 ,,	0·03324 ,,	..	0·6410	
	11.	21·25 H_2	Nil	21·25 H_2	0·00191 H_2	353·5	0·3722	194·7*
	12.	45·69 ,,	0·50	42·19 ,,	0·00407 ,,	705·5	0·7429	182·7*
IV.	13.	19·27 ,,	0·30	18·97 ,,	0·00171 ,,	279·8	0·2947	172·6*
	14.	10·14 ,,	about. (8·0)	?	?	42·0	0·0442	?
	15.	33·75 ,,	[24·74] 30·89	9·01 ,,	0·000811,,	52·5	0·0553	68·2
V.	16.	5·30 O_2	Nil	5·30 O_2	0·00758 O_2	220·3	0·2320	30·6
	17.	6·08 ,,	,,	6·08 ,,	0·00869 ,,	190·3	0·2004	23·1
	18.	5·24 ,,	,,	5·24 ,,	0·00750 ,,	166·8	0·1756	23·4
	19.	5·96 ,,	,,	5·96 ,,	0·00853 ,,	174·2	0·1834	21·5
	20.	5·52 ,,	,,	5·52 ,,	0·00789 ,,	163·6	0·1723	21·8
	21.	5·32 ,,	,,	5·32 ,,	0·00761 ,,	160·7	0·1692	22·2
	22.	5·98 ,,	,,	5·98 ,,	0·00852 ,,	155·4	0·1637	19·1
	23.	6·00 ,,	3·60	2·40 ,,	0·00343 ,,	38·5	0·0405	11·8
			Totals .	41·80 ,,	..	..	1·3371	

TABLE III.—Calorimetric Experiments on the Occlusion of Oxygen by Platinum Black (continued.)

Experiment.	Operation.	Gas.		Gas absorbed.		Calorimeter deflection.	Heat evolved. K = 100 gram. cal.	Heat evolved per gram of gas absorbed.
		Admitted.	Exhausted.					
		cub. centims.	cub. centims.	cub. centims.	grams.	millims.		K.
VI.	24.	115·05 H_2	[24·48] 32·43	90·57 H_2	0·00815 H_2	1260·0	1·3268	162·8
VII.	25.	4·79 O_2	Nil	4·79 O_2	0·00685 O_2	199·5	0·2100	30·6
	26.	60·76 ,,	[24·75]	36·01 ,,	0·05149 ,,	1012·8	1·0663	20·7
			Totals .	40·80 ,,	..	..	1·2763	
VIII.	27.	Oxygen occluded. Exhausted at a red heat		21·67 O_2	0·03098 O_2			

Let us consider first of all the first experiment of five operations. Starting with the platinum black prepared as above, successive quantities of oxygen were added until after Operation 5 it was fully charged up with oxygen. The absorption of the oxygen in the first three operations was very rapid, but became slower in the fourth and still slower in the fifth. The table sufficiently explains itself. In Operations 1, 2 and 3, the heat evolved per gram of oxygen absorbed remains pretty nearly the same. In Operation 4 there is a distinct diminution in the amount of heat evolved, whilst in 5 this has tailed off to 10 K. These results are remarkable. If all the numbers in the last column had remained constant, we might have concluded that we were dealing only with the direct occlusion of oxygen, or, even if the last two or three values had remained constant we might have accepted these as representing the heat of occlusion of oxygen. As it is, however, and knowing as we do that the platinum black, in spite of the treatment to which it was subjected, may have contained some platinum hydrogen, we must conclude that the first four numbers, at any rate, are composite numbers partially due to the heat of occlusion of oxygen and partially to the heat of formation of water. It might have been expected that the first charge of oxygen would have removed all the hydrogen existing in the platinum, and it is curious that for small concentrations of platinum hydrogen, the ratio of the quantity of oxygen which goes to form water to that which is occluded remains constant; for this is obviously what the approximate constancy of the first three numbers means. For greater concentrations of platinum hydrogen, as can be seen from Operation 16, this no longer holds good.

The net result of these five operations is to fix the upper limit of the heat of occlusion of oxygen at 10 K per gram. From the fact that in Operation 4 some oxygen was extracted from the tube, we may suppose that at this stage most, if not all, the hydrogen had been removed as water, and that the number 15·8 is obtained because the effect due to true occlusion preponderates over that due to the formation of water. From the smallness of the quantity of oxygen occluded in Operation 5, no great reliance can be placed on the value 10 K, taken singly, but in all probability we are dealing in this case with true occlusion.

In Operation 6, 47·59 cub. centims. of hydrogen were admitted to the experimental tube still in the calorimeter, the heat evolved per gram of hydrogen absorbed being 203·1 K. This number has an asterisk attached to it to signify that the results may be calculated in another way, namely, 47·59 cub. centims. = 0·00428 gram of hydrogen were absorbed, the heat evolved being 0·8698 K. Now, one gram of hydrogen on being burnt to water evolves 342 K, hence, if we assume that the whole of the 47·59 cub. centims. of hydrogen were oxidised to water, the heat evolved should be 342 × 0·00428 = 1·4645 K. If the difference, viz., 1·4645 − 0·8698 = 0·5947 K, represents the heat absorbed on removing 23·8 cub. centims. of oxygen from the platinum black, then the heat absorbed on the removal of one gram of oxygen will be 0·5947 ÷ 23·8 × 0·00143 = − 16·8 K. This number approaches those obtained in Operations 1–4, but, of course, has the negative sign. The assumption on which this number is calculated, viz., that the *whole* of the hydrogen added went to form water, cannot be justified, and hence this number cannot be regarded as the true amount of heat absorbed per gram of oxygen removed.

The 47·59 cub. centims. of hydrogen added in Operation 6 were less than what is theoretically required for the complete removal of the oxygen contained in the platinum black, and, consequently, before Operation 7 was started, the platinum black was in pretty much the same condition as before the first operation, except that in all probability it contained a larger proportion of platinum hydrogen, since it had not been shaken up or exhausted at 184° C. This possibly explains why the values of the heat evolved per gram of oxygen absorbed in Operations 7, 8, and 9 are higher than in the corresponding Operations 1, 2, 3, and 4.

In Operation 10 the platinum black was fully charged up. If this had been done in two stages, say, by adding 6 cub. centims. and then 1·64 cub. centims., the value for the last would probably have been much less than 14·4 K. The falling off in Experiment III. is otherwise very similar to that in Experiment I.

In the fourth experiment hydrogen was added in successive stages. During Operation 14, 10·14 cub. centims. of hydrogen were admitted, and on making connexion with the pump it was found that the vacuum was far from complete. Since the pressure within the apparatus was not known, it was impossible to estimate how much hydrogen was really absorbed, and how much was simply filling the experimental tube. About 8 cub. centims. altogether were pumped off. In Operation 15 the hydrogen was admitted at full atmospheric pressure. The volume of hydrogen required to fill the experimental tube is given in square brackets [24·74], whilst 30·89 cub. centims. were afterwards extracted, the difference between them having been removed from the platinum *in vacuo*.

Operation 15 is interesting, as the value 68·2 K represents the true heat of occlusion of one gram of hydrogen, which is in good agreement with the values formerly obtained, the mean of which was about 69 K.

Just as in the case of 6, Operations 11, 12, and 13 can be calculated in a similar way, and give the following values per gram of oxygen removed, if we assume that in each case the whole of the hydrogen is oxidised to water, and that none goes to form platinum hydrogen.

Operation 11	— 18·4 K	per gram of oxygen removed.
,, 12	— 20·1 K	,, ,, ,,
,, 13	— 21·3 K	,, ,, ,,

Experiment V. is similar to I. and III., except that we start in this case with platinum black, which has been fully charged with hydrogen, and from which all the hydrogen which comes off *in vacuo* at 0° C. has been removed.

For the first addition of oxygen a greater amount of heat is evolved, viz., 30·6 K, probably due to the relatively large formation of water compared with the quantity of oxygen really occluded. The last charge of oxygen gives out 11·8 K per gram of oxygen absorbed, and this seems to be due for the most part to the true occlusion of oxygen.

At this stage we intended to stop the series of experiments and to find out, by exhausting at a red heat, how much oxygen had actually been occluded in the last set of operations; but, since there was some uncertainty whether the water which was formed was itself occluded or absorbed by the platinum, producing heat changes, or whether it simply condensed on the inner walls of the experimental tube and on the platinum black, it seemed that some light might be thrown on this point by a slight alteration in subsequent experiments.

The high value, 30·6 K, was obtained in Operation 16: but before this experiment was performed, the platinum black previously charged with hydrogen was kept in communication with a P_2O_5 tube *in vacuo* for two days, in order to remove as much as possible of the water along with the hydrogen. In Operation 24 the platinum black was fully charged with hydrogen. [24·48] cub. centims. were required to fill the experimental tube, whilst 32·43 cub. centims. were pumped off as expeditiously as possible, in order to leave most of the water formed, which diffuses very slowly through the capillary tubing, in the experimental tube. In the next operation, 25, a small quantity of oxygen was admitted, but the value for the heat evolved per gram of oxygen absorbed was 30·6 K, which is identical with the value obtained in Operation 16, although in the latter case as much water as possible had been previously removed from the platinum before starting. This experiment is, perhaps, not quite conclusive, but we think, from the general behaviour of platinum black, that it had already, from the very beginning, absorbed or occluded its quantum of water, and that this is not affected by placing the platinum in a vacuum, or by condensing more dew on its surface.

This assumption was confirmed by surrounding the bulb of a BECKMANN thermometer in an ordinary calorimeter with 5 grams of platinum black, dried at 100° C. When the temperature had become steady, the platinum black was moistened with water at the same temperature, injected from the outer bath of the calorimeter, but no definite rise or fall of temperature could be detected.

After charging up fully with oxygen, in Operation 26, the experimental tube was removed from the calorimeter, the platinum black transferred to a hard-glass tube, exhausted at the ordinary temperature, and then heated to redness *in vacuo*. 21·67 cub. centims. = 0·03098 gram of oxygen were pumped off at a red heat, and this represents the amount of oxygen which was actually occluded in Operations 25 and 26.

So far we have not been able to obtain any very definite direct value for the heat of occlusion of oxygen, except that in Operations 5, 10, and 23 we found approximate values, viz., 10·0, 14·4, and 11·8 K per gram of oxygen occluded.

With the data which we possess, however, and knowing that during the last process of charging with oxygen 21·67 cub. centims. of oxygen were occluded, we can calculate the heat of occlusion indirectly.

(1.) In Experiment VII., 40·80 cub. centims. of oxygen were used, and of this 21·67 were actually occluded, whilst the remainder, 19·13 cub. centims., must have been burnt to water. Now, on combustion, 19·13 cub. centims. = 0·02735 gram oxygen should produce $\frac{684 \times 0{\cdot}02735}{16} = 1{\cdot}1695$ K. But, during the combustion, $2 \times 19{\cdot}13 = 38{\cdot}26$ cub. centims. = 0·003443 gram of hydrogen must have been removed from the platinum black, and since 69 K are absorbed on the removal of 1 gram of hydrogen, the removal of 0·003443 gram should absorb $0{\cdot}003443 \times 69 = 0{\cdot}2376$ K.

If, therefore, the heat of formation of water minus the heat absorbed on the removal of the hydrogen, *i.e.*, $1{\cdot}1695 - 0{\cdot}2376 = 0{\cdot}9319$ K, represents all the heat changes which take place, with the exception of the heat evolved or absorbed on the occlusion of 0·03098 gram of oxygen, then the difference between the actual heat developed, viz., 1·2763 K and 0·9319 K, *i.e.*, + 0·3444 K, represents the heat evolved on the occlusion of 0·03098 gram of oxygen, or 11·1 K are evolved per gram of oxygen occluded.

This number is in good agreement with those indicated by the preceding more direct measurements.

(2.) The amount of heat absorbed on the removal of oxygen from platinum black can be calculated in a somewhat similar way.

In Experiment VII., as we have just seen, 38·26 cub. centims. of hydrogen must have been left over occluded from the preceding Experiment VI. Besides this, however, 7·95 cub. centims. of hydrogen were pumped off *in vacuo* in Operation 24, so that in Experiment VI., altogether, 38·26 + 7·95 = 46·21 cub. centims. of hydrogen must have been occluded. The total hydrogen absorbed was 90·57 cub. centims.; hence 90·57 − 46·21 = 44·36 cub. centims. must have combined with 21·18 cub. centims. of oxygen occluded in Experiment V. to form water.

The evolution of heat corresponding to this formation of water is

$$44·36 \times 0·00009 \times 342 = 1·3652 \text{ K.}$$

Similarly, the heat evolved on the occlusion of 46·21 cub. centims. hydrogen is

$$46·21 \times 0·00009 \times 69 = 0·2869 \text{ K.}$$

The sum of the two heats evolved, viz., 1·6521 K, is greater than the heat actually evolved, viz., 1·3268 K, by 0·3253 K.

Consequently, 0·3253 K must have been absorbed on removing 22·18 cub. centims. = 0·03172 grm. of oxygen, and hence − 10·3 K were *absorbed* per gram of oxygen *removed*.

(3.) Going back another step, we find that, from Experiment VI., 22·18 cub. centims. of oxygen must have been occluded in Experiment V. The total oxygen used in Experiment V. was, however, 41·80 cub. centims., and therefore 19·62 cub. centims., = 0·02805 gram of oxygen, must have formed water with the corresponding quantity of hydrogen pre-existing in the platinum black, giving out

$$\frac{684 \times 0·02805}{16} = 1·1995 \text{ K.}$$

19·62 cub. centims. of oxygen would remove 39·24 cub. centims. of hydrogen, with the absorption of

$$39·24 \times 0·00009 \times 69 = 0·2438 \text{ K.}$$

The heat due to the formation of water and the removal of hydrogen is thus 1·1995 − 0·2438 = 0·9557 K, whilst the heat actually evolved was 1·3371 K. Consequently, 0·3814 K have been liberated on the occlusion of 0·03172 gram of oxygen; or 12·0 K were evolved for every gram of oxygen occluded.

All these calculations depend on the final measurement of the oxygen occluded, and consequently any error involved in this determination would be magnified at each step backwards.

We have thus obtained three values for the amount of heat evolved per gram of oxygen occluded, or, what in one case amounts to the same thing, viz., the heat *absorbed* per gram of oxygen *removed.*

From Experiment VII.	11·1 K per gram occluded
" " VI.	−10·3 K " removed
" " V.	12·0 K " occluded

The mean of the three is 11·1 K per gram of oxygen occluded, and the first of these, for reasons which have just been stated, is the most trustworthy. Deviations due to the magnification of any errors, are already apparent in the next two, although it is satisfactory to find that their mean is identical with the first. If it had been possible to obtain another pair of values, then from the method of calculation the fourth would probably have been less than 10·3, and the fifth greater than 12·0, although the mean might have approximated to 11·1 K.

Altogether, therefore, we have six determinations of the heat of occlusion of oxygen, three of which were obtained more or less directly, whilst the other three were indirect measurements, namely :—

From Operation	K.	From Experiment	K.
5	10·0	VII.	11·1
10	14·4	VI.	10·3
23	11·8	V.	12·0

Of these, 14·4 K is obviously too high, since the final amount of oxygen absorbed in Operation 10 is so large that it probably includes some heat due to the formation of water.

The mean of the other five determinations is + 11·0 K per gram of oxygen occluded, and we think, although from the nature of the experiments and the difficulties encountered in determining this constant it is scarcely so satisfactorily established as the corresponding number for hydrogen, this value may be accepted as a pretty fair approximation to the amount of heat evolved per gram of oxygen occluded, or referred to a gram-atom of oxygen + 176 K.

VI. *Speculations on the Nature of the Occlusion of Gases by Platinum Black.*

With regard to the occlusion of hydrogen and other gases by platinum black, we are not as yet in a position to form a definite opinion. The difficulties which lie in the way are considerable, and when we remember that the question, whether the much better defined product obtained by occluding hydrogen in palladium is to be regarded as containing the compound Pd_2H, or whether it is simply a solid solution of hydrogen in palladium, has not yet been definitely settled, it is not astonishing that the difficulties in deciding the corresponding question for the less well-defined product obtained by charging platinum black with hydrogen can not easily be surmounted. As far as we can see at present, the only solution to the problem is to be got by a more minute study of the physical properties of the substance.

It must be admitted that the inference which we have drawn, viz., that any given sample of platinum black occludes approximately the same volume of the different gases, seems to point to the conclusion that we are dealing with some phenomenon which is conditioned by the extent of the surface of the platinum black, as otherwise it is not quite clear why hydrogen, oxygen, carbon monoxide, and sulphur dioxide should all be absorbed in equal volumes. On the other hand, we have to deal with the equally significant fact that neither nitrogen nor carbon dioxide are absorbed except in comparatively small quantity. If, however, we confine our attention to the occlusion of oxygen by platinum black, the balance of the evidence which we can bring forward at the present time seems to indicate the formation of a definite compound or oxide.

If, in the first place, the occlusion of oxygen were merely the physical condensation of oxygen in the capillary pores of the platinum black, we should expect that raising the temperature would either have very little effect or would simply re-evaporate the condensed oxygen, whilst, as a matter of fact, rise of temperature is accompanied by increased absorption up to the temperature of about 360°–380° C., when the oxygen is again given off.

This behaviour seems to militate against the view that we are dealing with physical condensation or liquefaction in the pores. Solid solution however is not excluded; but if it be remembered that platinum black absorbs about 100 volumes of oxygen, whilst there is no authenticated case on record in which platinum in the concrete form has been known to absorb more than a few volumes at the outside, it would follow that, if we were really dealing with solid solution, platinum in *all* its forms should absorb approximately the same quantity of oxygen, although we would be quite prepared to find a different *rate* of absorption in the different forms.

If we admit the possibility that the different varieties of platinum may be allotropic modifications, then the above arguments would not necessarily hold good, as may readily be seen by a comparison of the properties of red and yellow phosphorus. Carbon bisulphide may be regarded as being soluble in the yellow variety, but insoluble in the red, since it is purely a conventional matter which we call the solvent and which the dissolved substance.

In connexion with the view that the absorption of oxygen by platinum black may simply be due to superficial oxidation, we made a few experiments with the object of comparing the general behaviour of platinum black charged with oxygen with the lowest oxide of platinum. Several samples of platinous hydrate $Pt(OH)_2$ were prepared by boiling a dilute solution of potassium platinochloride K_2PtCl_4 with the theoretical quantity of caustic potash according to the method recommended by

Julius Thomsen. We were never able to obtain the platinous hydrate perfectly free from chlorine in this way, and we were surprised to find that after drying at 100° C. it always contained more than the theoretical amount of oxygen, and that the oxygen appeared to increase with the time taken in drying. On heating at higher temperatures in a current of dry air, still further quantities of oxygen were absorbed, but between 237° and 360° oxygen is again lost, reminding one of the behaviour of platinum black which begins to give off its oxygen at about 360° under ordinary atmospheric pressure.

Platinous hydrate appears to lose the bulk of its water at about 200°–250° C., and the oxide PtO so formed, begins to give off its oxygen very slowly at 380° *in vacuo.* At 444° a large fraction of the oxygen may be slowly pumped off, as the following table shows, but for its complete removal ignition at a red heat is necessary.

First three hours at 444° . .	8·50	cub. centims. extracted.
Second day „ „ . .	15·45	„ „ „
Third „ „ „ . .	2·50	„ „ „
Fourth „ „ „ . .	1·39	„ „ „
Fifth „ „ „ . .	1·02	„ „ „
Sixth „ „ „ . .	0·63	„ „ „
Exhausted at 460° . .	4·56	„ „ „
„ „ a red heat . .	6·68	„ „ „
	40·73	

A previous analysis of the same sample showed that 41·01 cub. centims. should have been obtained.

Platinum black and platinous oxide in general appear to behave in pretty much the same way, except that when heated *in vacuo* the oxygen comes off the oxide proper more slowly and at a slightly higher temperature.

Although some important evidence might lead us to suppose that the absorption of oxygen by platinum black is simply due to the superficial oxidation of the finely divided metal, the question cannot yet be regarded as definitely settled.

What is either a very curious coincidence or the best argument in favour of the view that the occlusion of oxygen is simply superficial oxidation is to be found in Thomsen's[*] determination of the heat of formation of platinous hydrate.

According to Thomsen the reaction

$$\mathbf{Pt} + O + \mathrm{H_2O} = \mathbf{Pt(OH)_2} + 179\ \mathrm{K}$$

takes place with the evolution of 179 K for 16 grams of oxygen, whilst we found that the occlusion of the same quantity of oxygen by platinum black was accompanied by the evolution of 176 K, the water which is a necessary factor in the above reaction being always present in platinum black.

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[*] J. Thomsen, 'Thermochemische Untersuchungen,' vol. 3, page 429.