PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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

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Phil. Trans. R. Soc. Lond. A 1895 **186**, 657-693
doi: 10.1098/rsta.1895.0019

XIX. *On the Occlusion of Oxygen and Hydrogen by Platinum Black.*—Part I.

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Received June 13,—Read June 20, 1895.

CONTENTS.

I. *Introduction.*

THE word "*occlusion*" was first used by GRAHAM,* to signify the absorption of, or shutting up, of gases in solid substances. Many porous bodies, such as charcoal, possess this property, and it is also to be met with among the metals, pre-eminently among the metals belonging to the eighth group of the Periodic Table, and especially among the platinum metals.

Platinum in the coherent state, and also in the state of sponge, has been very fully investigated by GRAHAM, in his classical researches. A large number of observations on platinum black are also on record,† but these, for the most part, have been made with impure material, and the results are often contradictory.

* GRAHAM, 'Phil. Trans.,' 1866, 399; see also 'Chem. and Phys. Researches,' 1876, p. 263.

† *Cf.* the Dictionaries by GMELIN-KRAUT, LADENBURG, DAMMER, &c.

21.10.95.

Our object has been to prepare platinum black in as pure a state as possible, and to subject it to careful examination. As is well known, platinum black is the most active form of platinum, it is a powerful oxidising agent, readily inducing so-called "catalytic actions." Discovered in 1820, by EDMUND DAVY,* it was thought by him to be platinous nitrite. DÖBEREINER,† BERZELIUS,‡ and ZEISE§ considered it a sub-oxide of platinum, whilst LIEBIG|| pronounced it to be nothing but the very finely divided metal. How far LIEBIG was right will be seen during the course of this investigation, the results of which we now beg to lay before the Society. In modern times BERTHELOT and others have worked with platinum black, but a discussion of their work is reserved for a later part of this communication.

II. *Repetition of Graham's Experiments.*

Before proceeding to the description of our experiments on platinum black, we may state that a few experiments were made with platinum foil and platinum sponge. The foil which we used was obtained from Messrs. JOHNSON, MATTHEY and Co., and was said to be pure. It weighed 51 grms. and was about $\frac{1}{1000}$ inch in thickness. After being rolled up into the shape of a cylinder it was introduced into an experimental tube of hard glass, somewhat similar to that represented in fig. 2A. The temperature and pressure of the air in the experimental tube were noted, and from a subsequent determination of the capacity of the tube it was found, on exhausting the tube at the ordinary temperature by means of a SPRENGEL pump, that the volume of the air pumped out corresponded exactly to the amount of air contained originally in the tube. In other words, the platinum foil gave off no measurable quantity of gas when exhausted at the ordinary temperature. On heating the foil to a dull red heat, however, 1·04 cub. centim. of gas was extracted. Taking the density of the platinum foil as 21·5, this amount of gas corresponds to 0·4 vol. of gas given off, the volume of the platinum being taken as unity. The composition of the gas was as follows:—

	cub. centims.		vol.
CO_2	0·76	or	0·3
O_2	trace		trace
Unabsorbed by alkaline pyrogallate	0·28		0·1
	1·04		0·4

Pure dry hydrogen was then admitted to the platinum foil and left in contact with

* ED. DAVY, 'Phil. Trans.,' 1820, p. 108; 'Schweigg. Journ.,' 31, p. 340.
† DÖBEREINER, 'LIEBIG'S Annalen,' 14, p. 10.
‡ BERZELIUS, 'Schweigg. Journ.,' 34, 81.
§ ZEISE, 'Kongl. Danske Vidensk. Selsk. Forh.,' 1825, 26, 13.
|| LIEBIG, 'Pogg. Annalen,' 17, 102.

it for three days. On connecting the tube with the pump again it was found that no hydrogen was given off from the foil at the ordinary temperature, and only a trace at a red heat. The platinum foil was next kept in contact with hydrogen for three hours at a red heat, and then allowed to cool down gradually in an atmosphere of the gas, but the same result was obtained. It was then charged twice with pure dry oxygen, once at the ordinary temperature and again at a red heat, but no appreciable quantity (0·1 cub. centim.) of gas could be pumped off.

GRAHAM found that the amount of hydrogen occluded by platinum depended largely on the texture of the sample employed. The following volume of hydrogen he found were occluded by unit volume of platinum.

Platinum wire (from fused platinum) .	0·128 — 0·207	vols.
Wrought platinum (old crucible) . .	3·83 — 5·53	,,
,, ,, (old tube) . . .	2·28 — 2·80	,,
Platinum sponge	1·48	,,

It will be seen from these numbers that the least absorptive form of platinum is the wire made from fused metal, but its absorptive power is greater than the foil examined by us. It is also very remarkable that wrought platinum occludes about three times as much hydrogen as platinum sponge. As it was conceivable that the texture of our platinum foil might be altered by alternately charging it with hydrogen and oxygen electrolytically, it was placed in dilute sulphuric acid and made to serve as the negative and positive pole alternately during the electrolysis of the acid. It was finally charged with hydrogen, washed with distilled water, dried in the steam bath, and then replaced in the experimental tube. No gas was given off *in vacuo* at the ordinary temperature, but at a red heat 1·20 cub. centim., equal to 0·5 vol., were extracted. This gas suffered no diminution of volume on being treated with caustic potash and alkaline pyrogallate, and caught fire on applying a small flame. It was probably hydrogen, and shows that platinum foil charged with hydrogen may be exposed to the air and heated in a steam bath without the whole of the hydrogen being oxidised to water by the oxygen of the air. The former experiments were now repeated, but it was found that the occlusive power of the platinum foil had not altered by alternately charging it with oxygen and hydrogen electrolytically.

A similar set of experiments was now made with platinum sponge, 44·2 grms. = 2·06 cub. centims. of platinum sponge, prepared by igniting platinum black at a red heat, were introduced into the experimental tube. After charging with oxygen and hydrogen practically no gas was given off *in vacuo* at the ordinary temperature. The following results were obtained :—

Oxygen.

	Oxygen extracted *in vacuo* at a dull red heat.
Charged with O_2 at a red heat for several hours, and allowed to cool down gradually	4·6 cub. centims. = 2·1 vols.
Charged a second time	4·9 ,, = 2·4 ,,

Hydrogen.

	Hydrogen extracted *in vacuo* at a dull red heat.
Charged with H_2, 3 days at ordinary temperature	1·4 cub. centims. = 0·7 vols.
,, ,, for one night	0·9 ,, = 0·4 ,,
,, ,, at a red heat, and cooled gradually	6·5 ,, = 3·1 ,,
,, ,, ditto ditto.	5·2 ,, = 2·5 ,,

The results with hydrogen are rather surprising, inasmuch as platinum sponge occludes more hydrogen when it is heated in the gas and then allowed to cool down gradually than when it is simply allowed to remain in contact with the gas at the ordinary temperature.

It will be seen later on, that platinum black behaves in precisely the opposite manner. If the sponge is left in contact with the hydrogen for a sufficiently long time it may, however, as the experiments seem to indicate, take up the same quantity of hydrogen as when it is heated. The action of the heat may thus be simply to increase the rate at which absorption takes place.

Another series of experiments was made with sponge prepared by igniting ammonium platinichloride.

The sponge weighed 9·15 grms. and its volume was taken as 0·44 cub. centim. As will be seen from the following numbers, its occlusive power for both oxygen and hydrogen was less than that of the first sample of sponge. Initially it was found to be charged with 0·39 cub. centim. = 0·9 vol. of a gas which was not further investigated.

	Gas exhausted *in vacuo* at a red heat.
Charged with H_2 at a red heat.	0·3 cub. centims. = 0·7 vol.
,, ,, at ordinary temperature .	0·2 ,, = 0·4 ,,
,, O_2 at a red heat.	0·2 ,, = 0·4 ,,
,, ,, at ordinary temperature .	0·25 ,, = 0·5 ,,

GRAHAM also made some experiments with the view to determine the influence of temperature on the absorption of hydrogen by platinum. Thus he found that a sample of platinum foil charged with hydrogen for three hours at 230° C., contained 1·45 vol. of hydrogen, whilst the same sample left in contact with hydrogen for the same time at 100° C., had only occluded 0·76 vol. of hydrogen. This agrees with what we have also found for platinum sponge.

III. *Preparation of Platinum Black.*

The best method of preparing platinum black is as follows:—100 grms. of hydrogen platinichloride are dissolved in about two litres of distilled water and boiled. After neutralizing with sodium carbonate, the boiling solution is slowly poured into a boiling solution of about 100 grams of sodium formate in two or three litres of water. Violent effervescence takes place, and the platinum is precipitated as a black powder, which is then thoroughly boiled out about eight or ten times with distilled water, the water in each case being separated by decantation. On one occasion, the platinum black was boiled out with dilute acids and alkalis. This process is, however, not to be recommended, as the dried substance on heating *in vacuo* gave off corrosive vapours which attacked the mercury of the pump and consequently had to be redissolved and reprecipitated in the usual way. The platinum black drained as free as possible from water is then dried either in a steam bath at 100° C. or over calcium chloride at the ordinary temperature.

Platinum black prepared in this way is a fine, black, impalpable powder and can be poured from one vessel into another like precipitated silica. It ought to be carefully preserved from all traces of grease and volatile matter. In all the experiments which we have made with it, ordinary greased taps and india-rubber joints have been avoided as much as possible. Taps can be lubricated with slightly deliquesced phosphorus pentoxide, and after a little practice glass tubes can be joined together before the hand blow-pipe about as easily, and much more securely, than by means of rubber tubing and wire.

IV. *The Water retained by Platinum Black.*

LIEBEG stated that platinum black was nothing else than finely divided platinum. Qualitatively speaking, this may be quite true, but we have never yet succeeded in preparing platinum black free from, firstly, water; and secondly, oxygen and traces of carbon dioxide. It is impossible, even by means of phosphorus pentoxide *in vacuo*, to completely remove the water below a temperature of at least 400° C., about which temperature the platinum black begins to pass into platinum sponge.

In order to see whether the amount of water given off, or the amount of water retained, by platinum black *in vacuo* at different temperatures were constant, the following series of water determinations was made. The platinum black, dried at 100° C., was placed in a hard glass tube connected with a weighed U-tube, containing phosphorus pentoxide, which was attached to the pump. A vacuum was then produced in the apparatus whilst the platinum black was kept heated at the required temperature until all the water had been taken up by the phosphorus pentoxide.

The increase in weight of the tube gave the amount of water directly. The following table gives the percentage amount of water given off by the platinum black at the different temperatures. Three different preparations of platinum black were used, and it will be seen that they contained about 0·5 per cent. of water, and that about one half of the total quantity of water was given off *in vacuo* at 130° C.

Temperature.	1st preparation.	2nd preparation.	3rd preparation.		
	I.	II.	III.	IV.	V.
°	per cent.	per cent.	per cent.	per cent.	per cent.
130	..	0·26	0·21	..	..
237	..	..	0·33	..	..
280	..	..	..	0·40	0·38
320	..	..	..	..	0·43
330	..	..	..	0·46	..
360	..	..	..	..	0·47
410	..	..	..	0·49	..
440	..	..	0·43	..	..
650 (?)	0·54	0·46	0·45	0·52	0·49

From these figures it would be fair to assume that at any given temperature the amount of water retained by platinum black is constant.

V. *The Density of Platinum Black.*

During the course of this investigation it was frequently necessary to know the volume occupied by a given weight of platinum black. A determination of its density was therefore necessary. This was made in the usual way with a pyknometer specially constructed for the purpose. After the platinum black was introduced into the pyknometer it was half filled with distilled water and connected with a pump. The water, with the platinum black suspended in it, was then boiled, in order to get rid of all traces of air adhering to the powder. After the pyknometer had cooled down to the ordinary temperature again it was filled up to the mark with boiled distilled water. The accurate adjustment of the water level to the mark was made after the temperature 25° C. had been attained by plunging the pyknometer into a thermostat at 25° C.

Weight of platinum black taken	11·4811 grms.
,, pyknometer and water, at 25° C. . . .	16·3099 ,,
,, ,, ,, + platinum black .	27·1989 ,,

The loss of weight of the platinum black in water is thus 11·4811 + 16·3099 − 27·1989 = 0·5921 grm., and hence the density of platinum black at 25° C., compared with water at the same temperature, is 11·4811 ÷ 0·5921 = 19·4.

The platinum black, however, contained 0·552 per cent. of water, and if we calculate the density of dry platinum black, which still, however, contains oxygen, as will be seen later on, we get for the loss of weight in water

$$11{\cdot}4117 + 16{\cdot}3099 - 27{\cdot}1989 = 0{\cdot}5287 \text{ grm.},$$

and for the density 25°/25°

$$11{\cdot}4177 \div 0{\cdot}5287 = 21{\cdot}6,$$

or, compared with water at 4° C., 21·5.

As it is only necessary to know the density in order to translate the results of actual experiments into volumes of gas given off or occluded by unit volume of platinum black, the density 21, which is sufficiently near for the purpose, has been used throughout to effect the comparisons.

VI. *The Absorption of Oxygen by Platinum Black.*

As has already been stated, platinum black invariably contains a considerable quantity of oxygen which has no doubt been absorbed or occluded from the air during the process of washing or drying. Platinum black prepared in the way described in Section III. takes up no more oxygen on being exposed to an atmosphere of this gas for several days. The object of the following series of experiments was to determine the total quantity of oxygen and carbon dioxide contained in platinum black, and also to ascertain how much of these gases was given off *in vacuo* at different temperatures. For this purpose the platinum black dried at 100° C. was heated *in vacuo* in a hard glass tube A (fig. 2, p. 668), at first to moderate temperatures by means of the vapour jacket F, and finally to a red heat. The experimental tube A was attached to the pump and the rest of the apparatus by a ground glass joint B, lubricated with phosphoric acid, and further protected by a little mercury poured into the thistle-shaped enlargement at the top. It is bent as shown in the figure, and is supposed to lie in front of the plane of the paper in order to prevent the upward current of hot air from acting prejudicially on the ground joint and the taps. The washing and drying tubes shown in the figure, with the exception of the tube E, which was filled with phosphorus pentoxide to dry the gas evolved, may be left out of consideration. Before beginning an experiment, the capacity of the experimental tube, together with that of the narrow bore tubing between the taps C and D, was first of all determined by pumping out the air and measuring it at the same temperature and pressure as that which obtained when the taps were shut previous to exhausting the apparatus up to the tap D. After introducing the platinum black, the true capacity of the experimental tube was then found by subtracting the volume of the platinum black from the capacity of the tube as determined in the above way. On now exhausting the tube A, containing a known quantity of platinum, it was found that no measurable amount of gas was given off from the platinum black at the ordinary temperature *in vacuo*. The platinum black was then heated successively at the different temperatures given in the following tables until no more gas was given off. It was found that the gas consisted chiefly of oxygen. At low temperatures (up to 237°), almost pure carbon dioxide along with a trace of nitrogen or some other gas not absorbed by alkaline pyrogallate was however evolved. Frequently, a slight explosion* or sudden swelling up of the platinum black was noticed in the neighbourhood of 300° C., but the cause of this is unknown, and in no case was the explosion accompanied by a large evolution of gas. In the following tables the temperatures are contained in the first column; the second and third columns contain the amount, in cubic centimetres, of carbon dioxide and oxygen respectively given off. In the last column are tabulated the number of volumes of oxygen given off by unit volume of platinum black. All the gas measurements contained in this communication are reduced to 0° C. and 760 millims., unless otherwise stated.

I. Platinum Black taken, 5·1187 grms. = 0·244 cub. centim.

Temperature.	CO_2.	O_2.	O_2.
°	cub. centims.	cub. centims.	(vols. Pt. = 1).
17 { 0·0			
100 { 0·0			
184 { 0·74 }†	0·67	2·97	12·2
237 { 0·83			
280 { 2·07			
340	..	15·07	61·8
400	..	2·30	9·4
650 (?)	..	0·55	2·2
		Total . . .	85·6

* *Cf.* Descotils, 'Gilb. Annalen,' 27, 231.

† In this experiment the total gas given off up to the temperature 280° C. was analysed all together.

II. PLATINUM Black taken, 5·2380 grms. = 0·249 cub. centim.

Temperature.	CO_2.	O_2.	O_2.
°	cub. centims.	cub. centims.	(Vols. Pt. = 1).
18	0·0	0·0	0·0
100	0·82	0·02	0·09
184	2·73	0·06	0·24
237	0·08	0·53	2·13
280	..	1·44	5·78
360	..	8·19	32·89
440	..	5·15	20·68
650 (?)	..	2·56	10·28
		Total . . .	72·09

III. PLATINUM Black taken, 5·0754 grms. = 0·242 cub. centim.

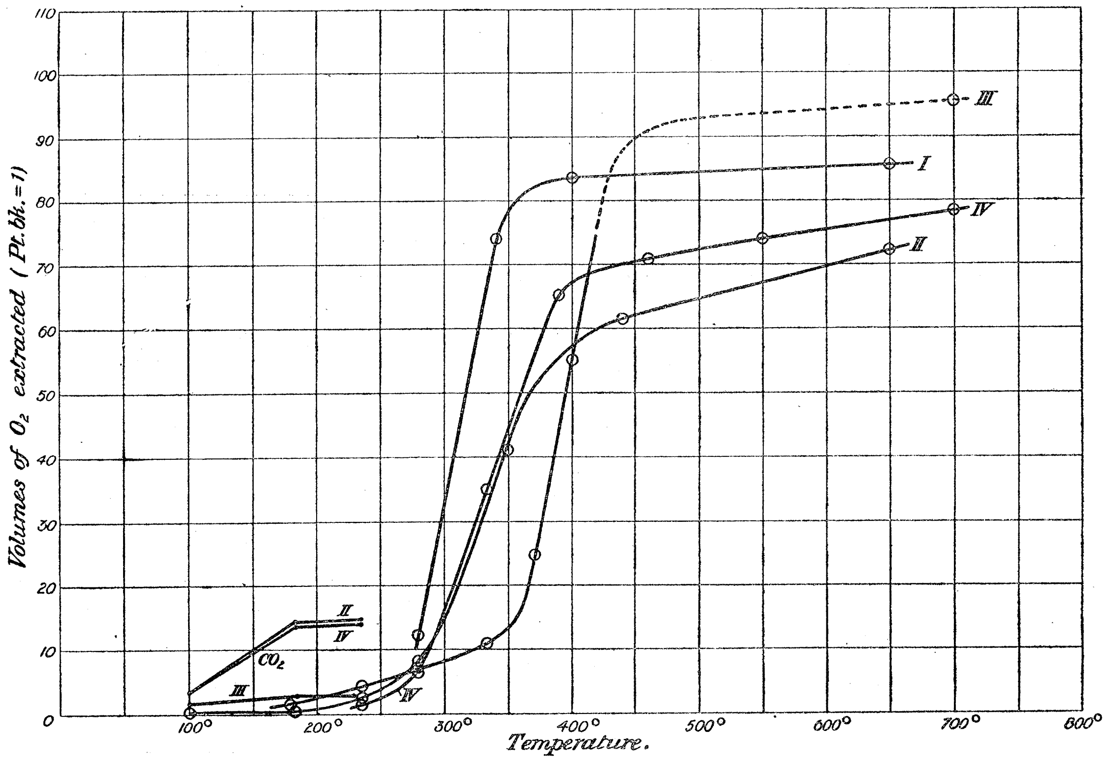
Temperature.	CO_2.	O_2.	O_2.
°	cub. centims.	cub. centims.	(Vols. Pt. = 1).
18	0·0	0·0	0·0
100	0·40	0·0	0·0
184	0·32	0·37	1·53
237	0·05	0·65	2·69
280	..	0·75	3·10
333	..	0·88	3·64
370	..	3·36	13·88
400	..	7·48	30·91
700 (?)	..	9·63	39·79
		Total . . .	95·54

IV. PLATINUM Black taken, 5·8069 grms. = 0·277 cub. centim.

Temperature.	CO_2.	O_2.	O_2.
°	cub. centims.	cub. centims.	(Vols. Pt. = 1).
18	0·0	0·0	0·0
100	0·94	0·0	0·0
184	2·74	0·0	0·0
237	0·24	0·41	1·48
280	..	1·30	4·69
335	..	7·92	28·59
390	..	8·46	30·55
460	..	1·37	4·95
550	..	1·03	3·72
700 (?)	..	1·22	4·40
		Total . . .	78·38

The results of the above experiments are plotted graphically in the accompanying curves, fig. 1, in which the ordinates represent the number of volumes of oxygen or carbon dioxide given off by unit volume of platinum black, and the abscissæ the temperatures. A glance at the above tables or curves shows that the oxygen begins

Fig. 1.



to come off about 200° C., that the evolution is very rapid between 300° and 400°, and that the bulk of the oxygen is given off a little above the latter temperature.

The following short table gives the total volumes of carbon dioxide and oxygen given off per unit volume of platinum black.

	CO_2.	O_2.	$CO_2 + O_2$.
I.	2·7	85·6	88·3
II.	14·18	72·09	86·27
III.	3·18	95·54	98·72
IV.	14·15	78·38	92·53

The numbers vary considerably, although the platinum black used in all four cases was taken from the same preparation, but it is very remarkable that when the amount of oxygen obtained is small (II. and IV.) the amount of carbon dioxide is large.

The curves representing the evolution of carbon dioxide are also shown in fig. 1, and if the amount of carbon dioxide is added to the quantity of oxygen extracted, curves are obtained which more nearly coincide. It is difficult to account for this. If the platinum black had got contaminated with traces of organic matter in any conceivable way, then possibly the carbon might annex some of the oxygen, and this would afterwards reappear as carbon dioxide. Carbon dioxide formed in this way would occupy the same volume as the original oxygen, and some weight is lent to this hypothesis by the fact that the sum of the oxygen and carbon dioxide is more nearly constant.

Platinum black, dried at 100° C., thus contains rather less than 100 volumes, or about 0·66 per cent. by weight of oxygen. The amount of oxygen contained in platinum black varies, however, in different samples, and seems also to depend largely on the temperature at which it is dried.

As regards the carbon dioxide contained in the four specimens of the same preparation of platinum black which have been examined, its amount seems to vary between about 3 and 14 volumes; but, as has already been suggested, the apparently larger quantities of carbon dioxide may possibly correspond to an accidental introduction of some carbonaceous impurity. The numbers representing the total absorption of oxygen by platinum black have been confirmed in a later section of this communication, using a different sample of platinum and an indirect method.

VII. *The Absorption of Hydrogen by Platinum Black.*

Platinum black, as is well known, possesses, in common with palladium, the power of absorbing or occluding considerable quantities of hydrogen. In view of the fact, however, that platinum black always contains a certain amount of oxygen, it is important, in determining its absorptive power, to distinguish between the amount of hydrogen which is really absorbed by the platinum black *per se*, and that which is simply burnt up to form water by the oxygen already contained in platinum black. In making experiments with a view to ascertain the absorptive power of platinum black, prepared in the usual way, for hydrogen, this has been steadily borne in mind.

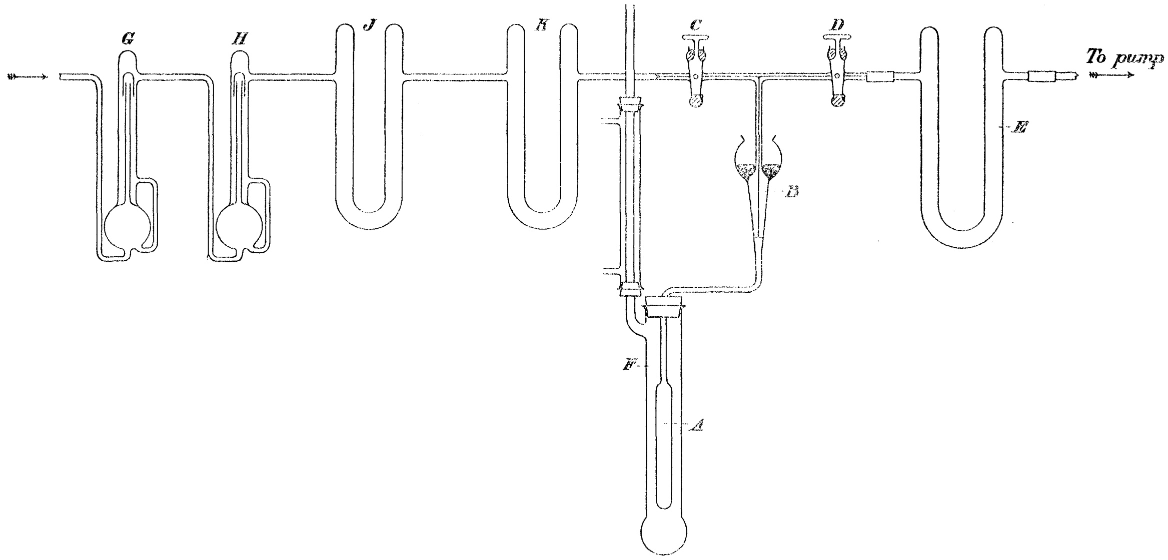
The apparatus which was used was essentially the same as that used for the determination of the oxygen in platinum black, with the addition of the washing and drying tubes shown on the left of fig. 2.

Hydrogen, prepared to begin with from pure zinc and pure sulphuric acid, was supplied by means of a KIPP's generating apparatus to the first washing tube, G (RICHARDSON's pattern),* containing a solution of potassium permanganate; it then passed through the next washing apparatus, H, charged with a solution of potassium hydroxide. Finally, the hydrogen was thoroughly dried by traversing the U-tubes,

* RICHARDSON, 'Trans. Chem. Soc.,' 1894, 469.

J and K, filled with fragments of solid potassium hydroxide and phosphorus pentoxide respectively.

Fig. 2.



The platinum black under investigation was placed in the experimental tube A, and the water which was pumped off was collected and weighed in the U-tube E. The tube E was attached to the apparatus by stout rubber tubing joints, which were securely wired. The hydrogen pumped off by the SPRENGEL pump at the different temperatures, and finally at a red heat, was collected and measured dry over mercury. Knowing, then, the amount of water originally contained in the platinum black, and the amount of water collected in E after charging with hydrogen, it was easy, from the difference of the two, to calculate both the amount of hydrogen which had gone to form water with the oxygen pre-existing in the platinum black, and also this amount of oxygen itself. As a check on these results, however, the total amount of hydrogen absorbed by the platinum black (independent of that required to fill the experimental tube A, of known capacity) was determined by introducing a gas burette, B, shown in fig. 11, p. 687, between the stopcock C, and the U-tube K.

In performing an experiment, the platinum black was first introduced into the experimental tube A, which was then rendered vacuous by means of the pump. The stopcock D was now shut, and the pure dry hydrogen slowly admitted in to the experimental tube A, through the stopcock C, until no more absorption took place. The bulk of the hydrogen was absorbed almost instantaneously, but, on allowing the stopcock to remain open for a few hours, a very slight additional amount of hydrogen was absorbed. The quantity of hydrogen filling the experimental tube at the ordinary temperature and pressure could easily be calculated from the capacity of the tube diminished by the volume occupied by the platinum black itself.

The following four tables contain the results obtained in four experiments made with the same preparation of platinum black, dried at 100° C. It will be noticed that platinum black charged with hydrogen behaves in a different manner from platinum black charged with oxygen, inasmuch as part of the hydrogen can be pumped off *in vacuo* at the ordinary temperature. The first column in the tables gives the temperatures at which the platinum black was heated. The lower temperatures were maintained by means of vapour jackets, whilst for the higher temperatures an air-bath was used, and the temperatures were determined either by a BALY and CHORLEY thermometer or by a LE CHATELIER thermo-electric junction. The second and third columns contain the total quantities of hydrogen given off, in cubic centimetres and volumes (platinum black = 1 vol.) respectively.

A. PLATINUM Black used, 5·3194 grms. = 0·253 cub. centim. Total hydrogen absorbed, 67·9 cub. centims.

Temperature.	Hydrogen exhausted up to temp. t.	
°	cub. centims.	Vols. (Pt. bk. = 1).
15	4·30	17·0
100	9·25	36·6
150	13·23	52·3
225	15·11	59·7
410	17·09	67·6
580	18·03	71·3

Water found, 0·0742 grm.

B. PLATINUM Black used, 5·3067 grms. = 0·253 cub. centim. Total hydrogen absorbed, 78·34 cub. centims.

Temperature.	Hydrogen exhausted up to temp. t.	
°	cub. centims.	Vols. (Pt. bk. = 1).
15	6·19	24·5
100	13·75	54·5
200	21·86	86·6
300	23·87	94·5
400	25·01	99·0
550	26·25	104·0

C. PLATINUM Black used, 5·1763 grms. = 0·246 cub. centim. Total hydrogen absorbed, 76·01 cub. centims.

Temperature.	Hydrogen exhausted up to temp. t.	
°	cub. centims.	Vols. (Pt. bk. = 1).
17	6·66	27·0
100	10·85	44·0
184	19·28	78·2
237	20·96	85·0
370	23·01	93·4
550	25·23	102·4

D. PLATINUM Black used, 5·1362 grms. = 0·245 cub. centim. Total hydrogen absorbed, 76·69 cub. centims.

Temperature.	Hydrogen exhausted up to temp. t.	
°	cub. centims.	Vols. (Pt. bk. = 1).
18	6·62	26·4
100	11·82	48·2
184	20·57	84·0
237	22·72	92·7
280	24·02	98·0
400	25·12	102·5
600	26·82	109·5

Water found, 0·0737 grm.

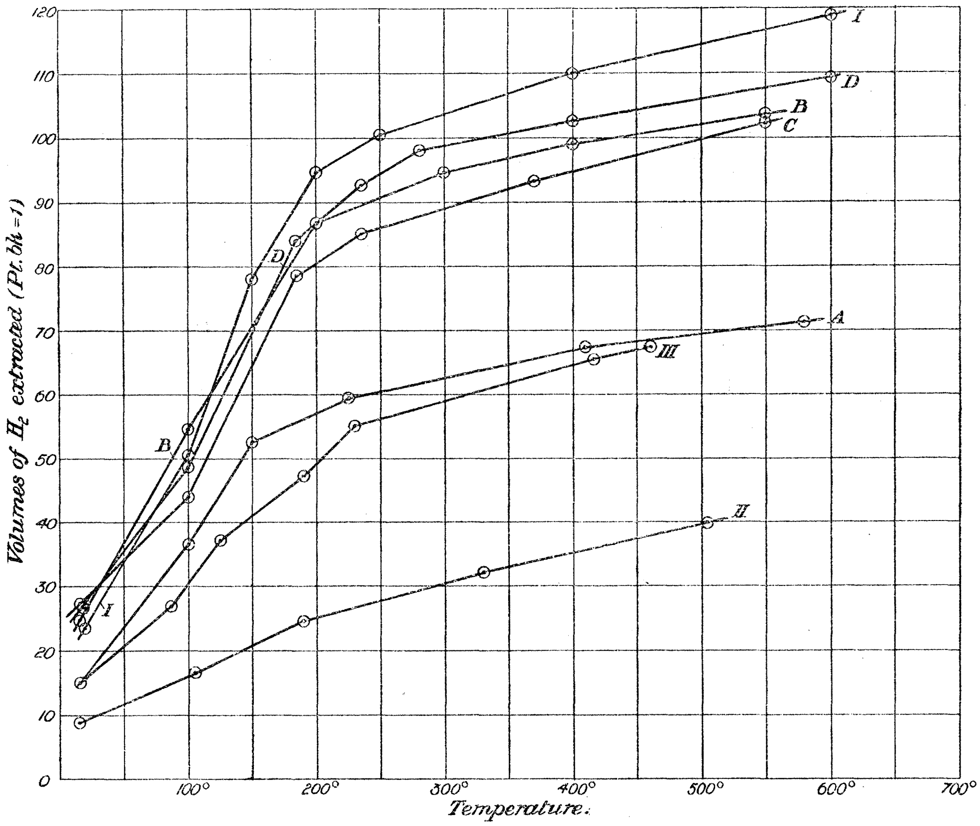
These results, together with three others, marked I., II., and III., are plotted graphically in the accompanying plate of curves. The ordinates represent the total number of volumes of hydrogen given off by unit volume of platinum black, whilst the abscissæ give the temperatures.

The Curves I., II., and III. were obtained from a different preparation of platinum black, and a slightly different method was used. Curve A is evidently too low, although the experiments were made as nearly as possible under the same conditions. In general, however, it is evident from a consideration of the curves that the hydrogen is more easily pumped off than oxygen, and that about five-sixths of the total quantity can be extracted about 300° C. It was also noticed that platinum black which had been charged with hydrogen was converted into platinum sponge at a lower temperature than platinum black which had not been so charged. The Curves B, C, and D are fairly concordant with each other and also with I. where a different sample of platinum black was used.

Neglecting A, the total amount of hydrogen absorbed in Experiments B, C, and D is:—

B.	C.	D.
309·7 vols.	309·1 vols.	313·0 vols.

Fig. 3.



Part of the total hydrogen absorbed, namely, that portion which has not gone to form water with the oxygen originally contained in the platinum black, is again evolved on heating to a dull red heat *in vacuo*. Assuming that all the rest has been converted into water in this way, an assumption which is justified by the results, we may construct the following table, which explains itself:—

Experiment.	Platinum black used.	Total hydrogen absorbed.	Hydrogen extracted *in vacuo* at a red heat.	Difference between last two.	Water corresponding to difference.	Water originally in platinum black.	Sum of the last two.	Total water found.	Difference (experimental error).
	grms.	cub. centims.	cub. centims	cub. centims.	grms.	grms.	grms.	grms.	grms.
A	5·3194	67·9	18·03	49·87	0·0404	0·0287	0·0691	0·0742	+0·0051
B	5·3067	78·34	26·25	52·09	.. ..	.. ..	.. ..	.. ..	.. ..
C	5·1763	76·01	25·23	50·78	.. ..	.. ..	.. ..	.. ..	.. ..
D	5·1362	76·69	26·82	49·87	0·0404	0·0277	0·0681	0·0737	+0·0056
I.	5·133	.. ..	29·15	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..
II.	5·236	59·2	9·90	49·30	0·0399	0·0242	0·0641	0·0601	−0·0040
III.	5·190	67·2	16·68	50·52	0·0410	0·0240	0·0650	0·0689	+0·0039

From the table it is evident that no matter what the absolute amounts of hydrogen absorbed and hydrogen evolved may be, the differences between the two are in all cases about 50 cub. centims. The slight variations in the weight of platinum black used do not appreciably interfere with this coincidence.

This 50 cub. centims. of hydrogen, even in the case of the apparently bad experiments A, II., and III., probably gets about 25 cub. centims. of oxygen from the platinum black to form water, and the amount of water capable of being formed in this way is given in the table. If to this amount of water we add the water originally contained in the platinum black, we get a number which corresponds as closely as can be expected with the total amount of water found.

Of the total absorption of hydrogen by platinum black, about 310 volumes, only about 110 (the maximum is 119) volumes are really occluded by the platinum *per se.*

The amount of oxygen originally contained in six of the above samples of platinum black, viz., A, B, C, D, II., and III., can be calculated in the following way.

The difference between the total hydrogen absorbed and the hydrogen finally extracted, tabulated in the fifth column of the above table, represents the amount of hydrogen which has been burnt up to water by the oxygen contained in the platinum black.

If we call this quantity n, then $n/2$ represents the quantity of oxygen contained by the platinum black, and $n/2v$, where v is the volume of the platinum black, the number of volumes of oxygen occluded by unit volume of platinum. The following values are thus obtained :—

A	contained	98·6	vols.	of oxygen.
B	,,	103·0	,,	,,
C	,,	103·2	,,	,,
D	,,	101·8	,,	,,
II.	,,	99·0	,,	,,
III.	,,	102·3	,,	,,

The direct determinations described in the previous section showed that platinum black contained rather less than 100 volumes of oxygen, so that the results obtained by the two different methods agree very well.

VIII. *The Influence of Diminished Pressure on the Absorption of Hydrogen by Platinum Black.*

The platinum black used for the following experiments had not such a high absorptive power for hydrogen as some of the samples previously examined. In the course of some other experiments it had been charged with hydrogen and exhausted at 130° C. It was then again charged with hydrogen at atmospheric temperature and pressure and exhausted at ordinary temperature. In this condition it still retained a large quantity of hydrogen. In order to see the effect of diminished pressure on the absorption of the rest of the hydrogen, the gas was admitted from a gas burette into the apparatus similar to that represented in fig. 2 until the required pressure was registered by means of a manometer which replaced the U-tube E, in fig. 2. The time allowed for charging ranged from 20 to 45 hours. The hydrogen contained in the manometer and pump was first pumped out and measured, then the gas filling the experimental tube A at the given temperature and pressure together with the hydrogen given off by the platinum black was extracted and measured. From these measurements and the amount of gas which had disappeared from the gas burette the following table was drawn up.

Column 1 gives the pressure at which the platinum black was charged with hydrogen.
Column 2, the hydrogen used as measured by the gas burette.
Column 3, the hydrogen contained in the experimental tube (calculated from the capacity of the tube and the temperature and pressure of the gas).
Column 4, the hydrogen contained in the manometer and pump. This gas was pumped out separately and measured directly.
Column 5, the amount of hydrogen actually absorbed, *i.e.*, the total hydrogen used, minus the sum of the volumes of the hydrogen contained in the experimental tube and pump.
Column 6 gives the amount of hydrogen extracted from the platinum black after subtracting the hydrogen contained in the experimental tube.

All the experiments were made at the ordinary temperature (about 19° C.) and the weight of the platinum black used was 7·96 grms. = 0·379 cub. centim.

Pressure.	Total hydrogen used.	Hydrogen contained in experimental tube (calculated).	Hydrogen contained in manometer and pump (found).	Hydrogen.	
				Absorbed.	Exhausted.
millims.	cub. centims.	cub. centims.	cub. centims.	cub. centims.	cub. centims.
767·0	38·05	17·94	17·12	2·99	3·05
371·4	17·68	8·69	6·08	2·91	2·90
176·5	9·42	4·14	2·51	2·77	2·78
30·9	3·46	0·72	0·42	2·32	2·31
11·1	2·26	0·26	0·22	1·78	1·80

As a check on these numbers, the platinum black was again charged with hydrogen, at ordinary temperature and pressure, and the gas pumped out fractionally at reduced pressures. 3·20 cub. centims. were required to charge the platinum black fully, and the following quantities were pumped off at reduced pressures.

Pressure.	Hydrogen extracted.
millims.	cub. centims.
416·9	0·00
264·5	0·59 (?)
125·7	0·38
59·5	0·21
22·4	0·39
0·0	1·89
	Total 3·46

The total hydrogen extracted exceeds that required for charging by 0·26 cub. centim.

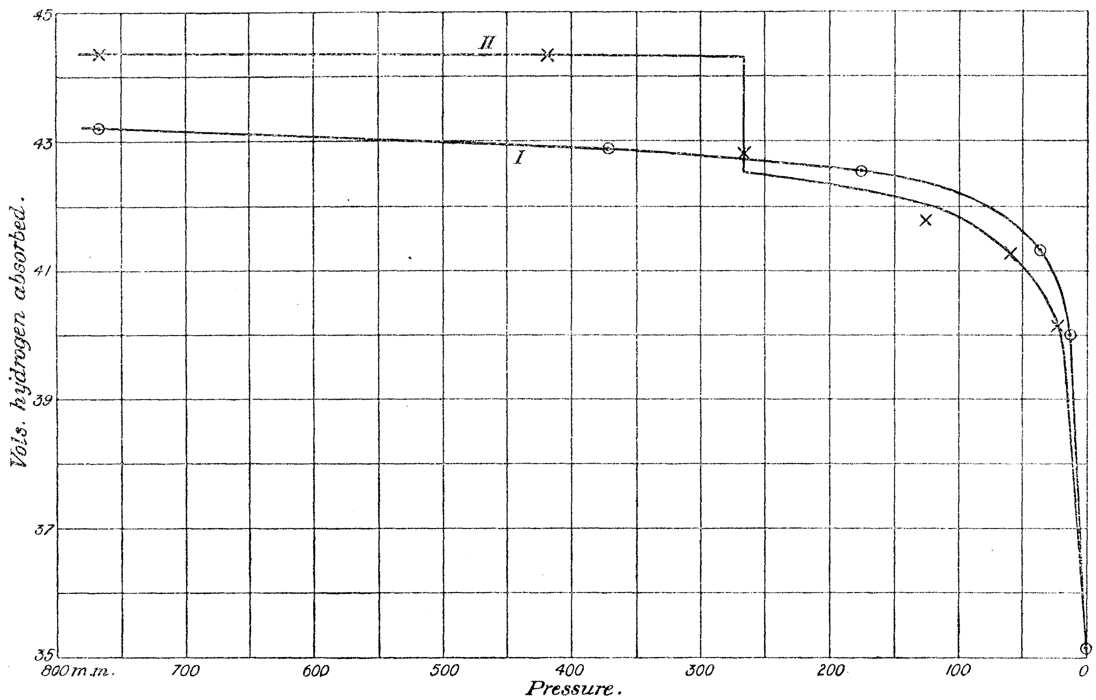
This is due to the fact that a slight leakage into the pump occurred at the pressure 264·5, so that the quantity pumped off at this pressure (0·59) is certainly too high.

The platinum black exhausted at the ordinary temperature gave off 13·14 cub. centims. = 35·13 volumes of hydrogen when heated to dull redness. We are, therefore, in a position to draw up the two following tables, which show the effect of diminished pressure on the absorption of hydrogen by platinum black. In the first series of experiments the mean of the hydrogen absorbed and hydrogen exhausted is used.

I.			II.		
Pressure.	Hydrogen absorbed.		Pressure.	Hydrogen absorbed.	
millims.	cub. centims.	vols.	millims.	cub. centims.	vols.
0·0	13·14	35·13	0·0	13·14	35·13
11·1	14·94	39·95	22·4	15·03	40·19
30·9	15·45	41·31	59·5	15·42	41·23
176·5	15·92	42·56	125·7	15·63	41·79
371·4	16·04	42·89	264·5	16·01	42·81
767·0	16·16	43·20	416·9	16·60	44·38
			(767·0)	16·60	44·38

The results of these determinations are plotted graphically in fig. 4. It will be seen that diminished pressure has a certain but not very pronounced effect on the absorption of hydrogen by platinum black at pressures above 200 or 300 millims. Below this pressure, however, the absorption rapidly falls off, and then remains nearly constant again. In other words, platinum black *in vacuo* absorbs a certain amount of hydrogen. This particular sample absorbed 35 volumes of hydrogen, but if a better sample had been employed the curves would probably have been displaced upwards parallel to themselves or nearly so, until 35 had become about 75, as in the case of the best samples of platinum black. On increasing the pressure of the hydrogen up to about 300 millims. a further quantity is absorbed (with the best samples of platinum black this would be about 25 or 30 volumes). An increase of pressure now has no appreciable effect up to pressures slightly above the atmospheric pressure. The effect of higher pressures is reserved for the next section, but it would seem from the run of the curves that this would also have little or no effect on the amount of hydrogen absorbed. The break in curve II. corresponds to the leakage into the pump which has been already mentioned. As no oxygen can be pumped off platinum black charged with oxygen at the ordinary temperature, it was impossible to make a corresponding series of experiments on the influence of diminished pressure on the absorption of oxygen. The effect of increased pressure has, however, been observed and recorded in a subsequent section.

Fig. 4.



IX. *The Influence of Increased Pressure on the Absorption of Hydrogen by Platinum Black.*

In determining the influence of increased pressure on the absorption of hydrogen by platinum black, the method adopted was to enclose platinum black saturated with hydrogen at atmospheric temperature and pressure in a graduated tube containing excess of hydrogen, and then to increase its pressure by means of a column of mercury. If no further absorption takes place, then the product of the pressure and volume (PV) of the gas should remain constant. On the other hand, if PV diminishes with increased pressure, then it would be possible to calculate the amount of absorption from the diminution of PV.

The apparatus which we used for this purpose is represented in figs. 5, 6, and 7. Fig. 5 shows the apparatus ready for an experiment. The vessel A, to contain the platinum black, is sealed to a graduated and carefully calibrated glass tube B, which is connected with the tube C, into which mercury can be poured in order to raise the

Fig. 5.

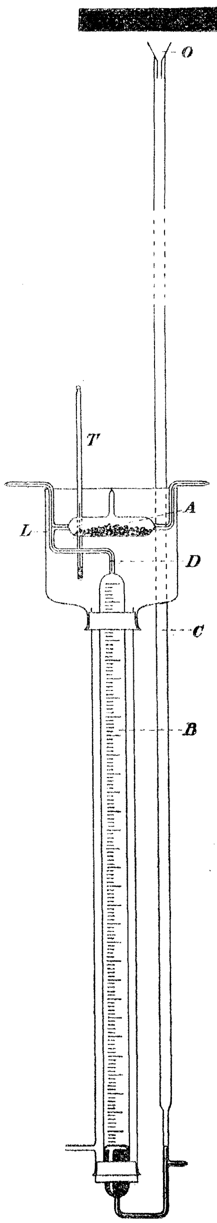


Fig. 6.

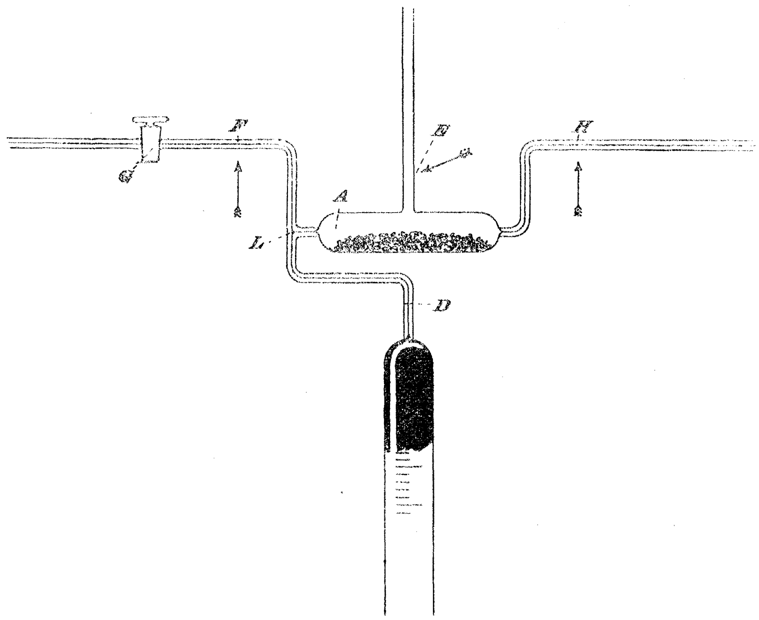
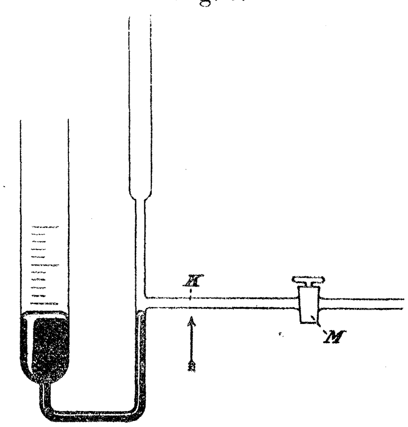


Fig. 7.



pressure. The graduations of the measuring tube or burette begin at the point D. After the experiments were at an end, the vessel A containing the platinum black was cut off from the graduated tube at the point D and its capacity separately determined. Knowing, then, the total volume of the hydrogen confined in the tube, its temperature being kept nearly constant by means of the water-jacket shown in the figure, and the height of the mercury column, it was easy to observe the product PV at the different pressures.

After the apparatus was fitted up and thoroughly dried, the platinum black was introduced through the tube E, fig. 6, which was then sealed off at the point E (indicated by an arrow).

The stopcock G being shut, some mercury was poured into the apparatus through the funnel O, fig. 5, and the tube H connected with a pump in order to produce a partial vacuum, so that no explosion would occur on allowing hydrogen to enter. When a sufficient vacuum was produced, pure dry hydrogen was passed into the apparatus through G. The whole apparatus was then filled with mercury, as shown in fig. 6, almost up to the point L.

The hydrogen thus swept out all the air from the vessel A, and in order to get rid of the excess of water formed, the current of hydrogen was continued for four hours. The exit tube was then sealed off at the point H. At this stage the stopcock M, fig. 7, was opened and the mercury allowed to flow out until it attained the level shown in fig. 7. The measuring tube was thus filled with pure hydrogen. As it was doubtful whether the stopcock M would withstand the high pressure (three-and-a-half additional atmospheres), it was sealed off at the point K, a long capillary being left in order to allow the mercury to flow out slowly after the experiments were completed.

The stopcock G was then shut and the apparatus allowed to stand overnight. As no further contraction in the volume of the hydrogen occurred, the apparatus furnishing hydrogen was sealed off at the point F.

The apparatus, with its water-jacket, then presented the appearance as shown in fig. 5. Successive quantities of mercury were now poured in through the funnel O and the height of the mercury column (measured with a steel scale and reduced to 0° C.), the volume of the gas and its temperature noted. When no further contraction occurred, another quantity of mercury was introduced and the corresponding readings taken. In this way the numbers recorded in the first three columns of the following table were obtained.

Temperature.	Pressure, millims. Hg. (0°).	Burette reading in millims.	Volume of hydrogen in cub. centims.	PV.	Volume of hydrogen in cub. centims. (0° and 760 millims.).
19·0°	765·8	682·0	136·8	97950	128·88
18·8	1222·7	388·9	85·5	97810	128·69
18·1	1664·5	255·0	62·7	97880	128·79
18·0	2507·1	131·3	41·6	97840	128·74
18·0	3415·2	66·3	30·5	97720	128·58

The next column contains the burette readings in millims., reduced to cub. centims. and increased by 14·6 cub. centims., the capacity of the vessel A down to the mark D. In the fifth column are tabulated the products of pressure and volume PV. The last column contains the volume of the hydrogen reduced to 0° C. and 760 millims. of mercury.

A glance at the table suffices to show that the product PV remains very nearly constant, and exhibits only a slight falling off (about 0·2 per cent.).

It is obvious, from the last column of the table, that by increasing the pressure of the hydrogen from one atmosphere to between four and five atmospheres, there is practically no change in the absorption of hydrogen by platinum black, since the reduced volume of the hydrogen at high pressure is only 0·3 cub. centim. less than at atmospheric pressure. As the platinum black used in these experiments weighed 5·972 grms., or had a volume of 0·284 cub. centim., it follows that only one additional volume of hydrogen was absorbed by unit volume of platinum black at the highest pressure.

X. *The Influence of Increased Pressure on the Absorption of Oxygen by Platinum Black.*

A corresponding series of experiments to those described in last section was now performed with oxygen. The apparatus and the method of charging it remained precisely the same. The quantity of platinum black employed was 5·979 grms. = 0·284 cub. centim., and the oxygen, made from pure potassium chlorate, was passed successively through sulphuric acid containing a little chromic acid, potassium hydroxide, and phosphorus pentoxide, before being introduced into the apparatus.

The results are given in the following table :—

Temperature.	Pressure, millims. Hg. (0°).	Burette reading in millims.	Volume of Oxygen in cub. centims.	PV.	Volume of Oxygen in cub. centims. (0° and 760 millims.).
15°·0	819·3	616·9	125·4	99658	128·1
,,	1165·7	400·0	87·4	96577	127·1
,,	1642·4	252·6	62·0	96526	127·0
,,	2112·6	171·4	48·1	96323	126·7
,,	2739·0	105·6	37·0	96064	126·4
,,	3417·0	61·6	29·5	95553	125·7

It will be seen that the falling off in the values of PV is much more marked in the case of oxygen than in the former experiments with hydrogen. At the highest pressure the volume of oxygen is less than the original volume by about 2 per cent.

Altogether 2·4 cub. centims. of oxygen have disappeared, and this corresponds to an additional absorption of oxygen by the platinum black of eight-and-a-half volumes, by increasing the pressure from one atmosphere to four-and-a-half atmospheres.

Platinum black charged with oxygen is thus much more influenced by changes in the pressure of the gas than platinum black charged with hydrogen. In the latter case, as we have already seen, the influence of pressure is so slight, at least between the atmospheric pressure and four-and-a-half atmospheres, as to be almost negligable.

XI. *The Influence of Temperature on the Absorption of Hydrogen by Platinum Black.*

GRAHAM determined the absorptive power of platinum foil for hydrogen at a red heat, at 230° C. and at 100° C. and found that the higher the temperature the greater was the absorptive power of the foil. We found this statement to be true for platinum sponge also, but it is obvious that it cannot hold good for platinum black, since platinum black at a high temperature is converted into sponge, and this we know absorbs at most only a few volumes of hydrogen, while platinum black absorbs over 100 volumes at ordinary temperature.

The investigation of the absorptive power of platinum black for hydrogen at temperatures above the atmospheric, but still below the temperature at which it is converted into sponge, thus became a matter of great interest.

The sample of platinum black to be examined was charged with hydrogen at the ordinary temperature and pressure and then sealed up in an atmosphere of hydrogen in the manner shown in fig. 8. The volume of the hydrogen having been ascertained, heat was applied to the platinum black by jacketting with a convenient vapour. The new volume of the hydrogen, always kept approximately at atmospheric pressure, was then read off. If it were found that the new volume, on reduction to 0° C. and 760 millims. pressure, were less than or greater than the original volume when similarly reduced, then the difference between the two would represent the amount of absorption or expulsion of hydrogen directly.

The apparatus shown in fig. 8 was sealed on, by means of the dotted tube C, to an apparatus for producing pure dry hydrogen. The stopcock on the dotted tube C (not shown in the figure) was then shut and a weighed quantity of platinuum black introduced into the bulb A through the tube D. Previous to the introduction of the platinum black, however, a weighed quantity of glass wool was placed in the bottom of A in order to prevent the finely divided platinum from falling through the capillary tube into the graduated tube B. Since the whole of the tube B, together with the bulb A and a portion of the stem of D up to the mark F, had been carefully calibrated, the weight of each substance introduced into A was carefully noted, so that the necessary corrections for the volume of each could be made.

The level of the mercury having been lowered beneath the junction of the tube C with B, the stopcock already mentioned was opened and pure dry hydrogen passed through the apparatus for five or six hours, until the moisture which had condensed in the upper part of A and in D had been removed completely. A weighed glass thimble tube containing a weighed quantity of phosphorus pentoxide was then dropped

Fig. 8.

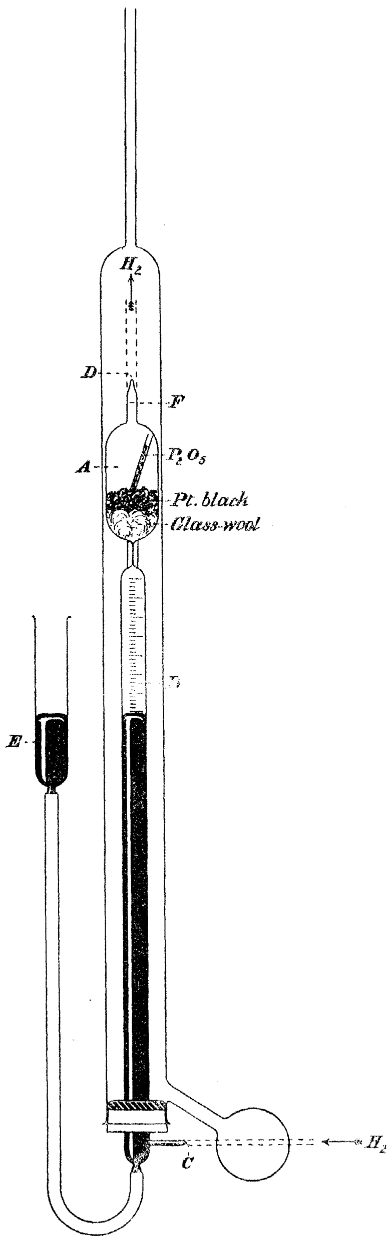
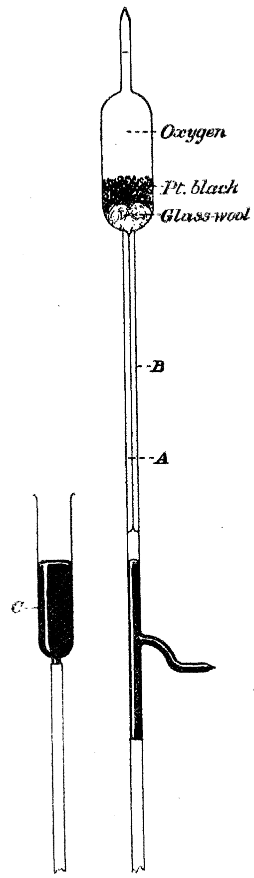


Fig. 9.



on the surface of the platinum black, so that any moisture given off on heating would be immediately absorbed and not interfere with the volume of the hydrogen. The open end of D was now connected with a narrow tube dipping under the surface of mercury and the current of hydrogen continued for another hour. At the end of

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this time the stopcock was shut and the side tube drawn off and sealed at the point C. When C had sufficiently cooled the mercury reservoir E was raised until the mercury level had nearly reached the top of the tube B. The upper tube D (the open end of which was still dipping into mercury) was then drawn off and sealed at the point D, a little way above the mark F. When the experiment was at an end the conical part of the tube above F was cut off, and its capacity determined separately.

The whole apparatus was then allowed to stand at atmospheric temperature and pressure for twenty-four hours in order to make sure that the absorption of hydrogen was complete. The volume of the hydrogen having been determined, the experimental tube was surrounded with a vapour jacket as shown in the figure. The volume, pressure, and temperature of the hydrogen was then noted for each different vapour-jacket. Each jacketting process had to be continued for at least a day before the volume became constant. Duplicate determinations, as will be seen in the following tables, were made at the temperature of boiling aniline in order to determine approximately the extent of the experimental error.

After each heating process the apparatus was allowed to stand over-night and a fresh observation taken in the morning in order to see how much of the hydrogen, if any, was re-absorbed on cooling.

The density of the phosphorus pentoxide, which does not seem to have been previously determined, was ascertained in the usual way by weighing in benzene. It was found to be 2·27, and it is further assumed that the deliquesced portion does not appreciably affect its volume. As the correction for the volume of the phosphorus pentoxide was itself very small we may consider this assumption justified. The total amount of correction of the capacity of A from all sources was 0·73 cub. centim., the initial reduced volume of the hydrogen being 33·40 cub. centims. The weight of platinum black was 4·6918 grms. = 0·22 cub. centim. The pressures are reduced to 0° C., and where necessary corrected for the vapour pressure of mercury and for the difference of temperature of the column of mercury heated in the vapour jacket.

The results are contained in the following table, those obtained after cooling being marked with an asterisk (*).

Temperature.	Volume.	Pressure.	Volume reduced to 0° C. and 760 millims. Hg.	Total hydrogen given off on heating.	
°	cub. centims.	millims.	cub. centims.	cub. centims.	volumes.
17·8	36·03	750·4	33·40	0·00	0·0
78·0	45·09	753·0	34·75	1·35	6·0
*18·1	36·13	753·5	33·60	0·20	0·9
131·7	58·26	802·2	41·50	8·10	36·3
*18·0	42·99	760·7	40·37	6·97	31·3
184·5	57·11	1027·3	46·07	12·67	56·7
..	50·11	1137·1	46·14	12·74	57·1
*19·0	48·62	760·0	45·46	12·06	54·1

The comparatively small variations in some of the above pressures from atmospheric pressure can have, as we saw during the investigation of the influence of increased pressure on the absorption of hydrogen by platinum black, no appreciable effect on the final result.

The table shows distinctly that on heating platinum black charged with hydrogen at ordinary temperature and pressure, a large proportion of the absorbed hydrogen is expelled, and that on cooling only a small fraction of this is re-absorbed, also that the higher the temperature at which the platinum black has been heated, the less is the amount of re-absorption.

It was impossible to determine the total quantity of hydrogen initially in this particular sample of platinum black experimented upon, but if we assume that it contained 110 volumes of hydrogen (this is about the average amount of hydrogen contained by the best samples of platinum black), then the quantity of hydrogen retained by the platinum black when heated in an atmosphere of hydrogen at different temperatures is as follows :—

Temperature.	Volumes of hydrogen retained by the platinum back.
°	volumes.
17·8	[110]
78·0	104
131·7	73·7
184·5	53·3

These results are plotted as Curve I, along with the results obtained with oxygen, in fig. 10, p. 685.

Arguing from these results we might expect to find that platinum black absorbs a still larger quantity of hydrogen when it is cooled down below the ordinary temperature.

As yet no experiments in this direction have been made, but we hope in a subsequent paper to be able to communicate the results of such experiments to the Society.

XII. *The Influence of Temperature on the Absorption of Oxygen by Platinum Black.*

Platinum black, charged with oxygen, was next heated in an atmosphere of oxygen. The experiments were conducted in precisely the same way as those just described, and the results are given in the following table :—

Temperature.	Volume.	Pressure.	Volume reduced to 0° and 760 millims.	Oxygen *absorbed* on heating.	
°	cub. centims.	millims.	cub. centims.	cub. centims.	vols.
17·0	31·32	751·8	29·17	0·0	0·0
78·0	37·87	755·0	29·27	−0·1	
* 16·0	30·78	750·3	28·71	0·5	2·2
131·6	39·40	753·0	26·34	2·9	12·5
* 17·8	30·02	698·3	25·90	3·3	14·2
182·9	39·41	728·2	22·62	6·6	28·4
* 15·5	30·13	590·7	22·16	7·0	30·2
237·1	36·77	708·9	18·36	10·8	46·5
* 18·0	30·87	487·8	18·59	10·6	45·7

A glance at the table suffices to show that the behaviour of platinum black when heated in an atmosphere of oxygen is totally different from the behaviour of platinum black charged with hydrogen and heated in an atmosphere of hydrogen. The latter gas is expelled on heating, whilst the former is absorbed.

The numbers are not quite so satisfactory as could be desired, for the platinum black on cooling (those experiments marked with an *) seems to absorb more gas (except in the last case). We believe, however, that this is only apparent. The phosphorus pentoxide employed to keep the gas dry got all used up about 78°, so that the gas was in all probability slightly damp, although nothing like saturated with aqueous vapour. At the high temperatures, therefore, the aqueous vapour would behave like a perfect gas, and an error would be thus introduced, that is, the true or reduced volume of the oxygen as calculated from the measurements at high temperature is probably too great on account of the presence of the aqueous vapour. At ordinary temperature the effect of the water vapour will in great measure have disappeared, and as it is extremely unlikely that more oxygen is absorbed on cooling, the volume of the gas measured at the ordinary temperature, after cooling down from the high temperature, is taken as representing more nearly the correct volume of the gas. The difference between the two, however, does not materially affect the general significance of the set of experiments.

The process of heating could not be carried farther then 237° C., because of the fact that at this temperature combination had just begun to take place between the hot mercury and the oxygen, a perfectly distinct ring of red oxide being visible within the graduated tube.

In carrying the heating to a higher temperature it was therefore necessary to slightly modify the apparatus.

At this stage the platinum black was transferred to a tube of hard glass, and the contents of the tube exhausted with the SPRENGEL pump. No gas was given off at the ordinary temperature, but at a red heat 111 volumes were liberated. Potash produced no diminution in the volume of the gas obtained, and it was practically all absorbed by alkaline pyrogallate. Of the 111 volumes given off, 46·5 volumes were absorbed on heating from ordinary temperature up to 237° C., hence the platinum black used in these experiments originally contained 111 − 46·5 = 64·5 volumes of oxygen. The low initial absorptive power of this sample of platinum black is accounted for by the fact that it had previously been used for another set of experiments, and had been charged alternately with hydrogen and oxygen.

Starting with platinum black containing 64·5 volumes of oxygen at the ordinary temperature (17°) the following table shows the amount of oxygen absorbed on heating at different temperatures in an atmosphere of oxygen.

Temperature.	Volumes of oxygen contained in platinum black.
° 17·0	64·5
78·0	66·7
131·6	78·7
182·9	94·7
237·1	111·0

These numbers are represented graphically in Curve II., fig. 10. The Curves I. and II. show very clearly the difference in behaviour of platinum black towards hydrogen and oxygen.

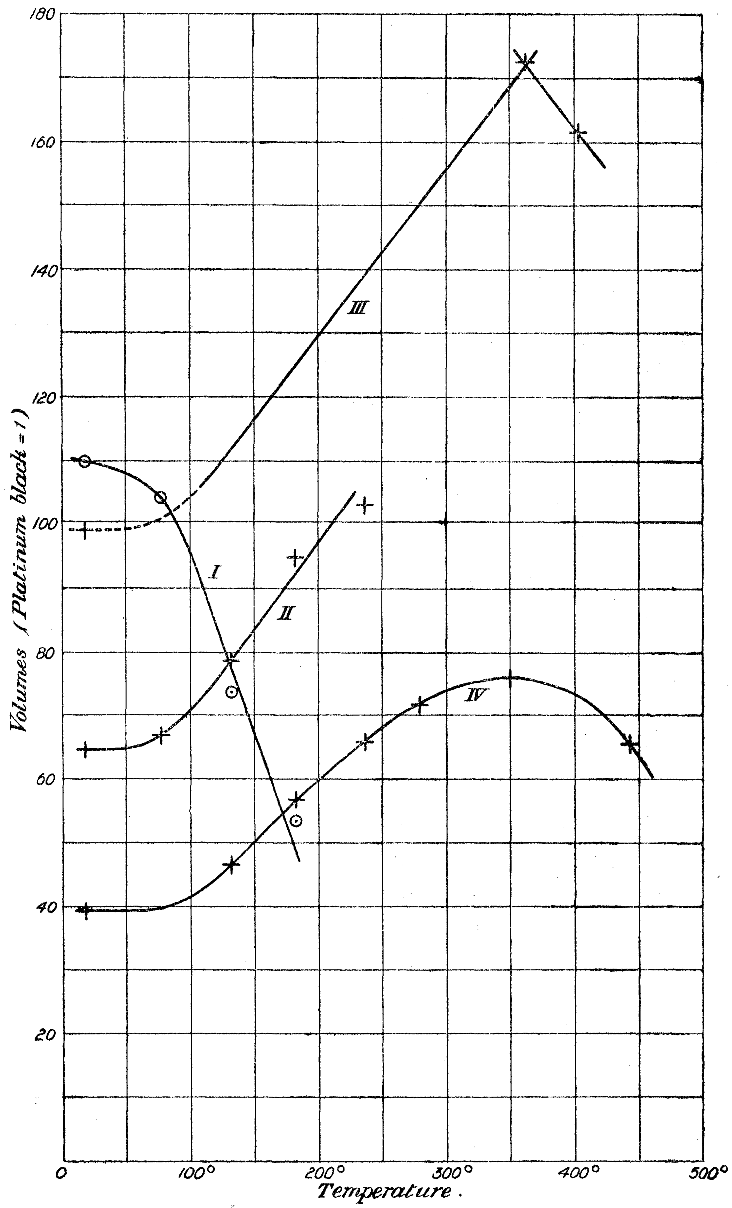
Knowing that platinum black is converted at a high temperature into platinum sponge, and that platinum sponge has a very low absorptive power for oxygen, we would expect to find a turning point in Curve II., or in other words it became important to determine the temperature at which there was a maximum absorption of oxygen.

For reasons which have been already alluded to, the apparatus in use was valueless for this purpose. The apparatus shown in fig. 9, p. 680, somewhat after the nature of a constant volume air thermometer, and constructed entirely of hard glass, was therefore made. In most respects it was similar to the apparatus last employed, but in place of the graduated glass tube B of fig. 8, the hard glass capillary tube AB was substituted. This tube had a mark A engraved on its stem, and the volume of oxygen contained in the bulb was always kept at constant volume by raising or lowering the mercury cistern C.

In the first experiments a hard glass thimble tube containing phosphorus pentoxide was also introduced into the bulb of the apparatus to keep the gas dry. This had soon to be abandoned, however, for reasons which will appear immediately.

In the first experiment a sample of platinum black containing initially 98·8 volumes of oxygen was employed. Heated in the presence of oxygen for a day at 362° C., 73·3 additional volumes of oxygen were absorbed. On heating for another day at 403° C., 9·2 volumes were *expelled*. Above this temperature, however, more oxygen was absorbed, and it was noticed that phosphorus pentoxide had distilled out of the small tube, and the results then became very irregular. Up to 403° C., the results are plotted roughly in Curve III., fig. 10, below.

Fig. 10.



Above this temperature they are no longer trustworthy, and on examination it was found that the platinum black, now converted into sponge, was contaminated with yellow brittle patches. It therefore occurred to us, that the phosphorus pentoxide had combined in some way with the platinum sponge, and that the compound then went on absorbing further quantities of oxygen, even up to a temperature of about 600° C.

Our suspicions were verified in the following manner. The platinum sponge containing the yellow patches was thoroughly boiled out with distilled water in order to remove all the free phosphoric acid. On fusing the residue with a mixture of potassium and sodium carbonates and a little potassium nitrate, and dissolving the fused mass in water, large quantities of phosphoric acid were found in the filtrate. Drying the gas with phosphorus pentoxide was thus rendered impossible, and subsequent experiments had to be conducted without it.

In the section of this paper dealing with the amount of water retained by platinum black, it was incidentally mentioned that platinum black is converted into platinum sponge at a temperature of about 400° C. We were therefore of opinion that the temperature of maximum absorption of oxygen could not differ much from this temperature, or at any rate could not exceed it.

Curve III. of fig. 10 indicates that the required temperature is less than 400° C., but, to make quite sure of the upper limit of temperature, a sample of platinum black was heated in an atmosphere of oxygen, kept at atmospheric pressure and in absence of phosphorus pentoxide, at 444° C., the temperature of boiling sulphur.

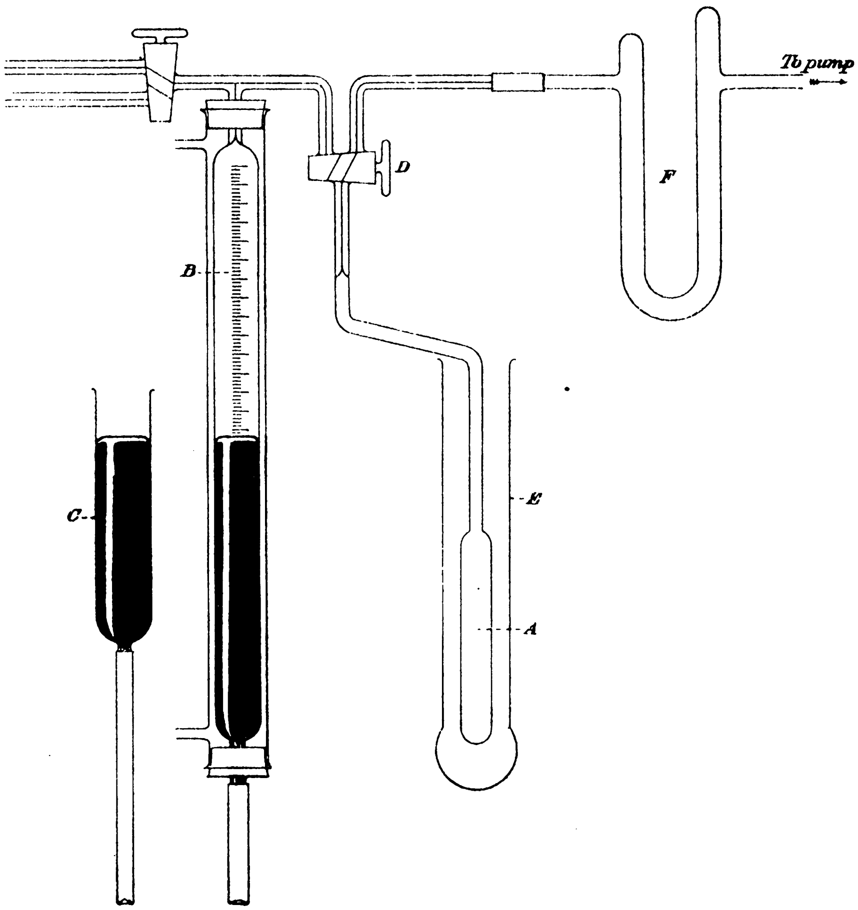
5·2766 grms. = 0·251 cub. centim. of platinum black, containing 98·8 volumes of oxygen, were placed in the experimental tube A, which was then sealed on to the gas burette B, as shown in fig. 11, p. 687. The platinum was then placed in communication with the pump and the phosphorus pentoxide tube F, by means of the three-way stop-cock D, and heated in a water-bath at 100° C., in order to get rid of as much water as possible. When the experimental tube was cold and vacuous, pure dry oxygen was admitted from the gas burette B, and the total volume of oxygen in burette and tube noted. The platinum was now heated in the sulphur-bath E, until the volume of oxygen in the gas burette remained constant, the pressure being always maintained approximately atmospheric by raising or lowering the reservoir C. After cooling, another measurement was made, and it was found that the oxygen in the burette and experimental tube had expanded 11·4 cub. centims. (0° and 760 millims.), *i.e.*, the platinum black had *given off* 45·6 volumes of oxygen at the temperature of boiling sulphur (444° C.).

The experimental tube of known capacity was then again connected with the pump. On exhausting at ordinary temperature, no gas was given off from the platinum black, but, on careful heating to dull redness, 15·1 cub. centims. = 60·4 volumes of oxygen, were extracted.

The results are given in tabular form below, and it will be noted that the sum of the volumes of oxygen given off at 444° C. and at a dull red heat amounts to 106 volumes, which is in fair agreement with 98·8, the quantity of oxygen originally contained in the platinum black, as determined by a direct experiment.

	Cub. centims.	Volumes.
O_2 evolved on heating platinum black in an atmosphere of O_2 under atmospheric pressure at 444° C.	11·4	45·6
O_2 still retained and given off at a red heat	15·1	60·4
Total	26·5	106·0

Fig. 11.

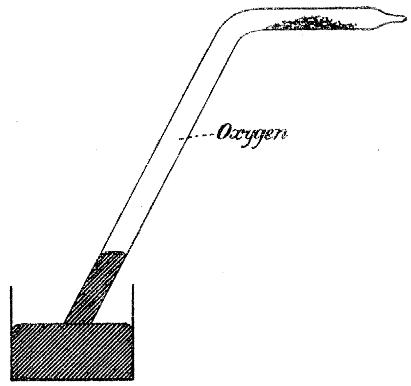


It was thus satisfactorily proved that the temperature of maximum absorption of oxygen was below 444° C., but, in order to determine *directly* whether the formation of a phosphorus compound of platinum was answerable for the abnormal absorption of oxygen already referred to, the following experiments were made :—

(1.) The experiment which has just been described may be regarded as the first of this series. It shows that, in absence of phosphorus pentoxide, platinum black does not go on absorbing oxygen indefinitely above 444° C., but in reality gives off at this temperature about 46 volumes of the oxygen originally absorbed.

(2.) As much phosphorus pentoxide as was used in the previous experiments (0·3 to 0·4 gram) was heated in an atmosphere of pure dry oxygen in the apparatus represented in fig. 12, to a temperature approaching dull redness. Only a minute fraction of a cubic centimetre was absorbed, hence the presence of a lower oxide of phosphorus in the phosphorus pentoxide has nothing to do with the abnormal absorption.

Fig. 12.



(3.) A similar experiment to the last was made, but the phosphorus pentoxide was replaced by a mixture of platinum black and phosphorus pentoxide. Almost the whole of the oxygen contained in the tube was rapidly absorbed at a dull red heat, the temperature being probably about 50° to 100° C. higher than the boiling-point of sulphur. Our suspicions regarding the formation of a phosphorus compound of platinum, perhaps phosphate or pyrophosphate, were thus fully confirmed.*

A new set of experiments, but with a different sample of platinum black, was therefore made without employing any phosphorus pentoxide to keep the gas dry. The platinum black was taken from an old preparation, as it was the only specimen available at the time, and subsequently it was found that it was rather an inferior one, containing only 39·4 volumes of oxygen. Although the absolute amount of gas absorbed is so low, this should in no way affect the turning point or temperature of maximum absorption of oxygen, as it has already been seen that the temperature at which practically all the oxygen or hydrogen (whether large or small in amount) is given off *in vacuo* from platinum black is always the same.

The experiments were made in the apparatus shown in fig. 9, p. 680.

Vapour jackets were used for heating up to the temperature 280° C., after which the capillary tube was bent at right angles at the point B, and the bulb then heated, first in the air bath, and afterwards in a bath of boiling sulphur, the vertical stem of the capillary tube being temporarily inclined in order to allow of the bulb being plunged in the sulphur bath.

* Since these experiments were made, Mr. BARNETT ('Chem. Soc. Trans.,' 1895, p. 513), working in Professor TILDEN's laboratory, has prepared platinic pyrophosphate, PtP_2O_7, by distilling phosphorus pentoxide over spongy platinum in a current of oxygen.—[Sept. 23, 1895.]

The results obtained are tabulated below.

I. PLATINUM black used, 5·6465 grams = 0·269 cub. centim.
Capacity of apparatus corrected, 18·76 cub. centims.

Temperature of heating.	Temperature of measurement.	Pressure corrected.	Volume reduced to 0° C. and 760 millims.	Oxygen absorbed.	
°	°	millims.	cub. centims.	cub. centims.	vols.
..	14·2	795·3	18·66	..	..
132	14·5	718·4	16·84	1·82	6·8
184	15·0	597·6	13·98	4·68	17·4
238	14·8	493·8	11·56	7·10	26·4
280	16·2	433·9	10·11	8·55	31·8
350	16·8	384·1	8·93	9·73	36·2
444	18·0	500·5	11·57	7·09	26·4

II. PLATINUM black used, 5·137 grams = 0·246 cub. centim.
Capacity of apparatus corrected, 17·85 cub. centims.

Temperature of heating.	Temperature of measurement.	Pressure corrected.	Volume reduced to 0° C. and 760 millims.	Oxygen absorbed.	
°	°	millims.	cub. centims.	cub. centims.	vols.
..	16·0	779·8	17·30	..	..
330	16·2	414·2	9·18	8·12	32·9
444	15·0	476·0	10·59	6·71	27·2

It is evident from these tables that absorption of oxygen takes place up to *at least* 350°, and that the temperature of maximum absorption lies between 350° and 444° C.

The original amount of oxygen contained in these samples of platinum black was 39·4 volumes, hence the total quantity of oxygen contained in the platinum black after heating in an atmosphere of oxygen at the undermentioned temperatures is as follows :—

I.

Temperature.	Oxygen contained in the platinum black.
°	vols.
18	39·4
132	46·2
184	56·8
238	65·8
280	71·2
350	75·6
444	65·8

II.

Temperature.	Oxygen contained in the platinum black.
°	vols.
18	39·4
330	72·3
444	66·6

The results of Experiment I. are almost identical with Experiment II., and have been plotted graphically in Curve IV., fig. 10, p. 685. A glance at the curve shows that the temperature at which platinum black absorbs the maximum quantity of oxygen is about 350° to 360° C. It is also interesting to note that this is the temperature at which most of the oxygen can be extracted from platinum black *in vacuo*.

The residual platinum black or sponge of Experiment II. was transferred to a tube of hard glass and heated to redness in vacuo. 15·78 cub. centims = 64·1 volumes of oxygen were given off, hence we have

	vols.
Oxygen originally in platinum black . . .	39·4
,, absorbed on heating to 444° . . .	27·2
Total	66·6

The total 66·6 vols. agrees fairly well with 64·1 vols. directly determined.

XIII. *Résumé and General Discussion of the Results.*

As far as our experiments on platinum foil and platinum sponge go, they may be said in general to confirm GRAHAM'S observations. At most, only a few volumes of oxygen or hydrogen are occluded by these substances.

The slight differences that do occur are no doubt due, as GRAHAM himself pointed out, to differences in the material experimented with.

Of recent work on the occlusion of gases by platinum foil, the most remarkable is that of BERLINER,* who arrived at results totally different from those obtained by GRAHAM and ourselves. According to BERLINER, ordinary platinum foil contains as much as from 71 to 227 vols. of occluded gas, and foil which has been deprived of this gas (not analysed) can afterwards absorb from 204 to 271 vols. of hydrogen and 100 vols. of oxygen. BERLINER invariably states the amount of gas absorbed or expelled directly in volumes referred to platinum as unity, and carefully avoids

* BERLINER, 'Wied. Annal.,' 1888, vol. 35, p. 791.

stating the amount of gas actually measured in cubic centimetres. From the table given on p. 807 of his paper, together with statements made on p. 803, we arrive at the following conclusions:—

(1.) The volume occupied by the *largest* sample of platinum foil with which he worked was 0·0043 cub. centim.; (2.) The *largest* volume of occluded or expelled gas which he measured never exceeded, and was usually much less, than one cubic centimetre; (3.) The graduated tube in which he measured his gas was not jacketed, and its temperature was only determined by thermometers suspended outside it. Although these thermometers were graduated in tenths of a degree C. and could probably be *read* to hundredths, yet we have no guarantee that they really indicated the temperature of the gas. A variation of 1° C. in his gas corresponded to a change in its volume of 0·116 cub. centim. and since the volume of the platinum foil was in general about 0·003 cub. centim., an error of one degree in the temperature of the gas means a difference in the occlusive power of 40 *volumes more or less;* (4.) An error of one millimetre in the measurement of the pressure of the gas similarly corresponds to an apparent occlusion of 14 *volumes more or less.*

Although working on a small scale with an apparatus such as BERLINER used has its advantages, *e.g.*, the surface of the platinum can be made and kept quite clean, and it can be heated to a very high temperature by means of an electric current, yet it has also very great disadvantages, as we have just seen, but until his results are confirmed by a less objectionable method, we must look upon them with great distrust.

In now passing on to the occlusion of gases by platinum black, we are obliged to neglect almost all the earliest observations, because they took no account of the oxygen it already contained, and mostly worked with an impure material, insufficiently washed free from accidental impurities, such as sugar, glycerol, alcohol, nitroso and chlorine compounds, &c. The former would give off large quantities of carbon dioxide, whilst traces of the latter give off corrosive vapours which attack the mercury of the pump. It has long been known that platinum black contained oxygen, but probably the first accurate determination was made by NEUMANN,* who found it to contain from 63 to 77 volumes. Most of the specimens which we examined, and which were dried at 100° C., contained approximately 100 volumes of oxygen, provided they had not been used previously for other experiments. Its density we found to be 19·4, or allowing for the water contained in the black, and which can only be got rid of by heating in vacuo to a temperature at which it no longer is platinum black but sponge, 21·5. LIEBIG estimated its density at 15·78, 16·32, and 17·572.

On placing the platinum black in an atmosphere of oxygen, and increasing the pressure of the gas to four-and-a-half atmospheres, only eight-and-a-half additional volumes were absorbed. Platinum black heated in an atmosphere of oxygen absorbs

* NEUMANN, 'Monatsh.,' vol. 13, p. 40.

a further quantity of oxygen up to the temperature 360° C. At higher temperatures, and under atmospheric pressure, the gas is again expelled. Most of the oxygen contained in platinum black can be extracted at about 400° C. in vacuo, but it requires to be heated to a red heat for its complete removal.

The amount of hydrogen occluded by platinum black independent of that required to form water with the oxygen already contained in it, is about 110 volumes for the best samples of black, the total amount of hydrogen absorbed being about 310 vols. This amount, however, is very largely influenced by the presence of traces of accidental impurities, probably grease, &c. An increase of pressure, up to four-and-a-half atmospheres, on platinum black already charged with hydrogen, only causes it to absorb one additional volume of hydrogen. A portion of the hydrogen occluded by platinum black can be removed at the ordinary temperature by means of the pump alone, but not until the pressure has decreased to about 300 millims. The bulk of the hydrogen can be extracted in vacuo at about 300° C., but a red heat is necessary for its complete removal. On heating platinum black charged with hydrogen in an atmosphere of hydrogen, a portion of the gas is immediately liberated, and in this respect it differs entirely from platinum black charged with oxygen.

We are not yet in a position to form an opinion as to whether we are dealing with true chemical compounds of these gases with platinum black, as maintained by BERTHELOT, or whether we are simply dealing with cases of absorption or of solid solution as suggested by VAN'T HOFF,* but we are at present engaged on experiments which we hope will throw some light on this subject.

BERTHELOT† is very definite in his statement that true chemical compounds of hydrogen and platinum having the formula $Pt_{30}H_2$ and $Pt_{30}H_3$ exist, and quite recently he again emphasised this opinion in an appendix to a paper by CAILLETET and COLLARDEAU.‡ According to these gentlemen a gas battery working under a pressure of about 600 atmospheres gives a much higher electromotive force and has a greater capacity than a similar battery working under ordinary pressure. Whether the increased efficiency is due to an increased absorption of gas under the high pressure was not, however, directly determined.

The evidence cited by BERTHELOT not only for the existence of definite chemical compounds of platinum with oxygen and hydrogen, but in particular for the compounds with hydrogen, having the extraordinary formulæ mentioned above is, in our opinion, insufficient to decide the question.

From the peculiar behaviour of the platinum black employed by BERTHELOT we conclude that it was by no means quite pure. For example, his moist platinum black gave off 21 per cent. of water at 100° C., and on heating to nearly 600° C *in vacuo* liberated nearly 200 volumes of oxygen and *less than one volume of carbon oxide,*

* VAN'T HOFF, 'Zeits. f. physikal. Chem.,' vol. 5, p. 322 (1890).

† BERTHELOT, 'Ann. de Chim. et de Phys.,' 1883, vol. 30, p. 519.

‡ CAILLETET and COLLARDEAU, 'Comptes Rend.,' vol. 119, p. 830.

besides nitrogen and oxides of nitrogen. The same sample after drying at 150° C. is said to have lost half its original quantity of oxygen. It then contained 90 volumes of oxygen and as much as 31 *volumes of carbon dioxide*, along with several other gases. Now we have already seen that platinum black absorbs more oxygen on heating, provided the temperature does not rise above 360° C., and we are unable to explain why BERTHELOT's platinum black lost oxygen, more especially as we found that even *in vacuo* the oxygen does not begin to come off until the temperature of about 300° C. is reached.

The heat which is evolved on the absorption of hydrogen by platinum black has been measured by BERTHELOT* and by FAVRE,† and has been used by BERTHELOT as an additional argument in favour of his formulæ. In view of the fact, however, that the heat due to the combination of the oxygen pre-existing in the platinum black with hydrogen is also included in these measurements, no safe conclusion can be drawn from these numbers. Until a sample of platinum black can be prepared free from oxygen and other impurities, or until the amount of oxygen contained in it has been properly allowed for, the numbers supposed to represent the heat of absorption of hydrogen by platinum black are of little value.

If a chemical compound of platinum and hydrogen exists at all we would from analogy prefer to look for a compound similar to Pd_2H, but as the existence of even this substance has been recently called in question,‡ we prefer for the present to leave the matter as it stands until sufficient data have been accumulated for an adequate enquiry.

* BERTHELOT, *loc. cit.*

† FAVRE, 'Comptes. Rend.,' vol. 77, p. 649; and vol. 78, p. 1257.

‡ HOITSEMA, 'Zeitsch. f. physikal. Chem.,' vol. 17, p. 1.

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