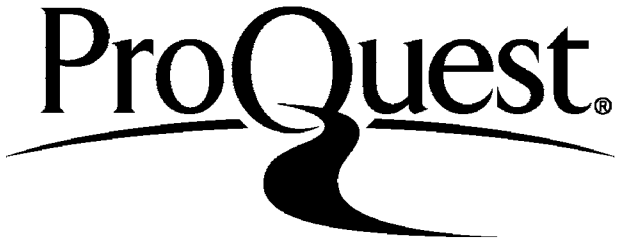
On the Origin of the Peculiar Glow obtained by heating Palladium in Gases at Low Pressures, and an Application of this Glow in an Investigation of the Disappearance of Gas under the Influence of the Induction Coil Discharge.

Thesis presented for the degree of M.Sc.
in the University of London by

Phyllis N. Lambert.

April, 1925.



On the Origin of the Peculiar Glow obtained by heating Palladium in Gases at Low Pressures, and an Application of this Glow in an Investigation of the Disappearance of Gas under the Influence of the Induction Coil Discharge.

In an investigation of the excitation of hydrogen by electronic bombardment, Prof.F.Horton and Dr.A.C.Davies (1) found that at a potential too low to excite the Balmer lines and the secondary spectrum, a blue glow persisted: and on spectroscopic examination of this blue glow, a continuous spectrum extending from the orange-yellow to the violet was observed. It was suggested that this continuous spectrum might be due to the combination of atomic hydrogen to form molecular, or perhaps triatomic, hydrogen. H.B.Lemon (2) also describes the appearance of a ~~continuance~~ continuous spectrum in hydrogen when the discharge was bright blue.

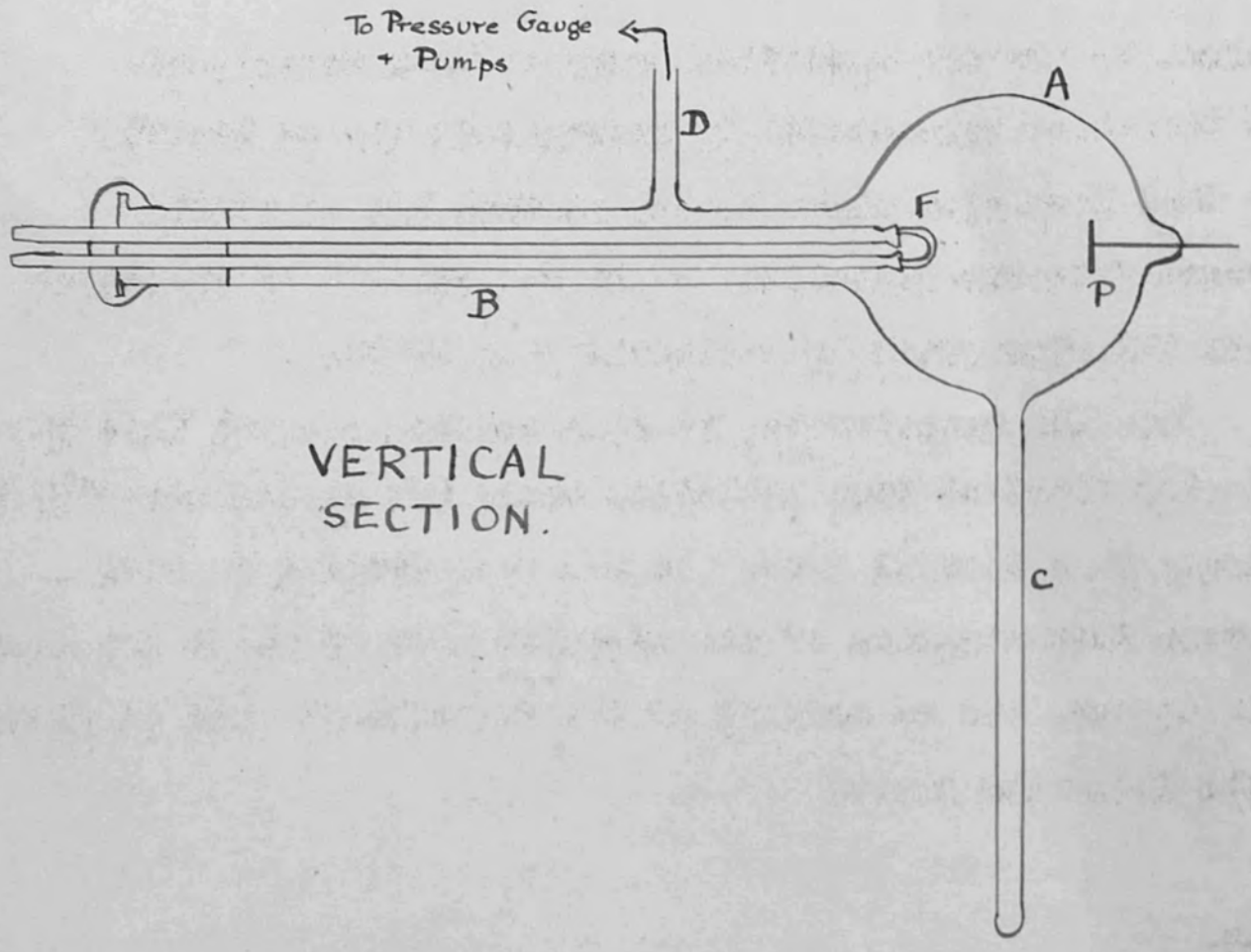
Now hydrogen is known to be occluded by palladium to a considerable extent, and probably the gas is contained in the metal in the atomic form, or at least it may be given up in the atomic form, since hydrogen from palladium is found to be especially active for a limited period of time. In 1909 the Rev.H.V.Gill(3) published an account of a blue glow

(1) Phil. Mag. xlvi. 1923.

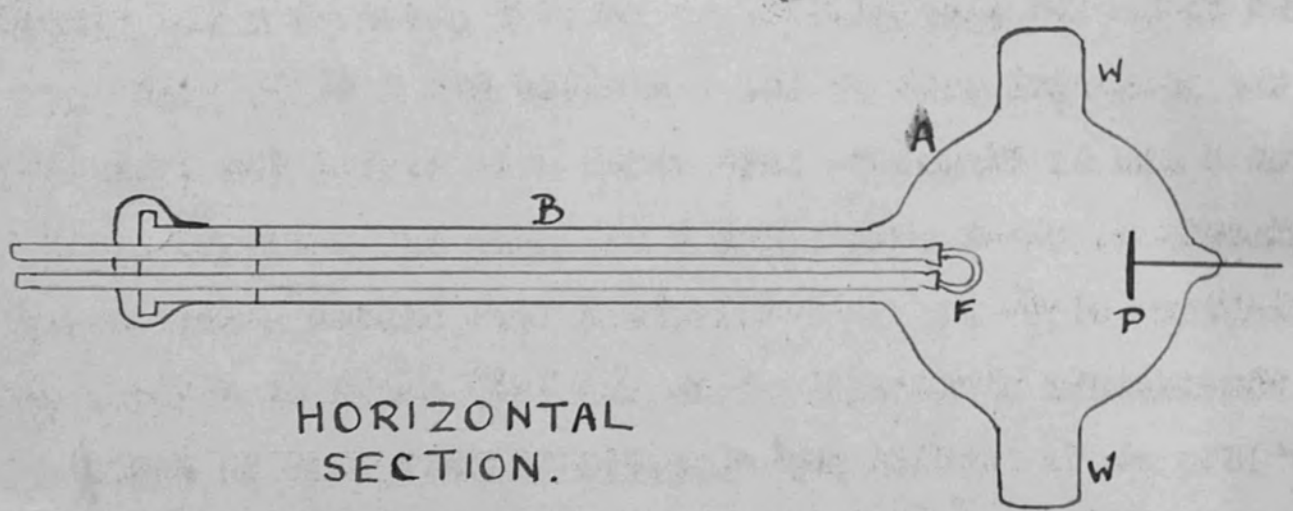
(2) Nature, Jan. 26. 1924, p. 127.

(3) Proc. Roy. Soc. 1909. p. 464.

DIAGRAM OF APPARATUS.



VERTICAL
SECTION.



HORIZONTAL
SECTION.

obtained by heating palladium under certain conditions. From the above experiments in hydrogen it seemed possible that this blue glow might be due in some way to atomic hydrogen from the palladium: so it was decided to re-investigate the glow given by palladium when heated.

From the experiments, it soon became apparent that the blue glow obtained from palladium could not be due entirely to hydrogen in a special form. It was then decided to make a thorough investigation of the circumstances in which the glow would appear; and an account of the experiments made is given in the following pages.

Apparatus.

The apparatus was constructed so that palladium filaments could be heated electrically in various gases at a low pressure. So the principal part of the apparatus was a glass bulb A, about 8 cm. in diameter, into which were sealed the palladium filaments F, which were about 2 cm. long and 2 mm. wide, and a platinum plate P. The filaments were heated electrically in the various gases with which the bulb could be filled. The platinum plate enabled an electric discharge to be passed across the tube by connecting it and the filaments to an induction coil. The spectrum of the discharge in the various gases was examined by a Hilger constant-deviation spectroscope.

To obtain the glow it was necessary to heat the palladium almost to its melting-point, so that frequently the filaments were burned out. Hence two filaments were mounted together; and to facilitate the mounting of new filaments ~~that~~ they were not sealed into the glass, but were attached by screws to the ends of three stout brass leads: the filaments had one common lead, but could be heated separately. The three leads passed through holes in an ebonite plug, and this was sealed by high melting-point sealing-wax into a side-tube B of the bulb. This side-tube was about 2·5 cm. in diameter, and 20 cm. long: the brass leads were made this length to ensure that there was no possibility of the heat of the filaments affecting the sealing-wax.

Sealed to the bulb was a vertical side tube C which could be surrounded by a flask of solid carbon dioxide or liquid air if required to freeze out water-vapour etc.

The palladium sputtered considerably on being heated, so that gradually the glass became blackened. Hence two extensions W,W were made, one on each side of the bulb: these did not get sputtered so that it was still possible to see the glow when the rest of the bulb was blackened.

The complete discharge-tube was connected by a side-tube D through a tap to a McLeod pressure gauge. This tap was always closed during experiments so that the discharge-tube

was isolated. The pressure-gauge was connected through another tap to a mercury diffusion pump which was backed by a Geryk oil-pump: this system would evacuate to a pressure of 1/100,000 mm. or less.

Between the gauge and the apparatus was a U-tube containing some glass-wool: this was always surrounded by solid carbon dioxide before opening the tap into the apparatus, so that no mercury vapour from the gauge ever entered it.

During the course of the experiments it was desired to fill the apparatus with certain gases: so there were sealed on near the pressure-gauge a small bulb containing potassium permanganate to give pure oxygen on gentle heating, a bulb of pure hydrogen, another small bulb containing a mixture of potassium bichromate and anhydrous sodium carbonate to give pure carbon dioxide on heating, and a bulb containing pure carbon monoxide: also there was a bulb of phosphorus pentoxide to dry the carbon dioxide.

The carbon monoxide was prepared by dropping concentrated sulphuric acid on to sodium formate, and heating gently. The gas was passed through a solution of caustic potash to remove traces of sulphur dioxide, and was then collected over distilled water. It was dried by passing through a U-tube immersed in liquid air before it entered the storage-bulb.

Thus the discharge-tube could be filled with air,

Oxygen, hydrogen, carbon monoxide or carbon dioxide, or any required mixture of these gases to any desired pressure.

Each time that new filaments were needed, the apparatus was cut down at the side-tube D, with the tap closed so that air did not enter the pressure-gauge. The ebonite plug was unsealed and removed: then the glass was well washed with concentrated chromic acid to remove the sputtered palladium, rinsed with tap and distilled water, and thoroughly dried. Two new filaments were mounted, and the ebonite plug sealed in: then the apparatus was sealed on again, and was pumped for a day to discover if there were a leak.

Experimental Results.

Under certain conditions, when the palladium filament was heated electrically almost to its melting-point, then a bright blue-purple glow appeared. The glow was about 2 cm. wide, and followed the shape of the filament, but it was separated from the filament by a distinct dark space.

Air.

A number of experiments were made in the air remaining in the apparatus after evacuating it to a pressure of about 1 mm. The range of pressures used was 1·70 to ·63 mm. The palladium filaments were kept at a dull red-heat for some time in order to expel the occluded gases, and were then

raised almost to melting-point to test whether the glow could now be obtained. But on no occasion was a glow obtained in air merely by heating the filament.

Then an electric discharge was passed across the tube for some time, it being passed in both directions. At first, the appearance of the discharge was a deep purple and pink, and the spectrum contained the usual nitrogen lines of the air spectrum and also the hydrogen lines H_α and H_β. But when the filaments were functioning as the cathode, the luminosity crept right up the brass leads, and then the appearance became gradually whitish. This was due to the production of carbon monoxide or carbon dioxide, the presence of one of these gases being shown by the appearance of the carbon monoxide bands in the discharge spectrum. Readings of a typical discharge-spectrum in air are given below.

I. Spectrum with Filament as Anode.

6563	-	very bright	-	H_α
5680	-	very faint	-	due to N_2
5207	-	faint	-	
5003	-	faint	-	due to N_2
4861	-	very bright	-	H_β
4709	-	bright	-	due to N_2
4277	-	bright	-	

II. Spectrum with Filaments as Cathode. (taken after I).

5611	-	faint band	-	due to CO
5199	-	very bright band	-	due to CO
4861	-	bright	-	H_β
4838	-	very bright band	-	due to CO
4709	-	faint	-	due to N_2
4566	-	very faint	-	
4518	-	very faint band	-	due to CO

N.B. The CO bands were sharp on the red side and diffuse on the violet, so the readings were taken on the sharp red side.

Thus the discharge-tube, after the passage of the discharge in residual air, contained hydrogen and carbon monoxide or dioxide in addition to oxygen and nitrogen. When carbon monoxide or dioxide had been produced in the tube, then on heating the filament, the glow appeared. This suggests that carbon monoxide or dioxide is required in the production of the glow.

In this mixture of gas, if a flask of solid carbon dioxide were placed on the side-tube C of the apparatus, after ten minutes it was sometimes found that the hydrogen lines had disappeared from the discharge-spectrum. When this

was the case, no glow could be obtained on heating the filament while the solid CO_2 was on the side-tube. On removing the solid CO_2 and allowing the tube to warm up, the glow was again seen on heating the filament, and H_β was again present in the discharge-spectrum. When however, H_β was still to be seen in the discharge-spectrum while solid CO_2 was on the side-tube, then the glow still appeared on heating the filament. Further, the behaviour was similar when liquid air instead of solid CO_2 was placed on the side-tube of the apparatus.

These experiments seem to indicate that hydrogen is necessary for the production of the glow. The fact that the cooling of the side-tube sometimes caused the disappearance of the glow, and sometimes did not, can be accounted for if the hydrogen were sometimes present simply as a constituent of water-vapour, which would be condensed out by the cooling. But water-vapour itself is not necessary, since the glow can be obtained when liquid air is on the side-tube, provided that hydrogen is present in a non-condensible form.

According to Gill's explanation of the production of the glow, water-vapour is necessary as well as hydrogen. But there is no evidence that he attempted to obtain the glow when hydrogen was present, but water-vapour was absent. In his experiment when liquid air ~~xxx~~ removed the water-vapour and caused the glow to fade, it was the removal of all

the hydrogen which was only present as a constituent of water-vapour, and not merely the removal of the water-vapour itself, which prevented the appearance of the glow.

From the experiments in air it therefore appears that hydrogen is necessary for the glow, and also probably carbon monoxide or carbon dioxide. In order to discover whether either of the gases oxygen or nitrogen, which were of course present in these experiments, is necessary, it was decided to exclude the nitrogen, and fill the apparatus with oxygen.

Oxygen.

Experiments, similar to those in air, were made in oxygen, the pressure usually being about 1mm., but varying on occasions from 2·30 to ·77 mm. The glow was never obtained merely by heating the palladium filaments; but to obtain it, it was always necessary to pass the electric discharge for some time. At first, the discharge-spectrum showed a few oxygen lines and H_β : but, as ~~mxkxxxx~~ above, during the passage of the discharge with the filaments as cathode, the carbon monoxide bands appeared as this gas or carbon dioxide was produced.

In several experiments the glow could not be obtained when solid CO_2 or liquid air was placed on the side-tube of the apparatus. But H_β was now missing from the discharge-spectrum, showing that the necessary hydrogen had been present only as a constituent of water-vapour, and was thus frozen out.

When a little hydrogen was admitted to the apparatus, then neither solid CO_2 nor liquid air had any effect on the glow. Hence water-vapour, as such, is not necessary for the glow. In fact the presence of an excess of water-vapour tends to prevent the appearance of the glow: for sometimes when the glow was not very bright, it was found that the placing of a flask of solid CO_2 on the side-tube caused a decrease of pressure, showing that water-vapour had been frozen out, and the glow now appeared very brightly on heating the filaments.

Finally, since the glow can be obtained in oxygen without any nitrogen being present, nitrogen is not necessary for the production of the glow.

Hydrogen.

Other experiments were made with hydrogen in the apparatus at various pressures between 1·27 and ·91 mm. The glow did not appear merely on heating the palladium filaments: but it appeared, usually quite quickly, on heating the filament after passing the electric discharge. At first, the discharge-spectrum consisted of a great number of sharp lines, the brightest being H_α, H_β and H_γ. But as carbon monoxide or dioxide was produced, the characteristic bands appeared in the spectrum, and then on heating the filament, a very bright glow was obtained.

The placing of a flask of solid CO_2 or liquid air on

the side-tube of the apparatus had no effect on the glow. This was to be expected since hydrogen was not present merely as a constituent of water-vapour.

On one occasion some oxygen was admitted to the apparatus after the glow had been obtained: but the glow was not thereby improved, in fact the glows obtained when most of the gas present was hydrogen, were some of the brightest ever seen.

If oxygen is required for the glow, then in the experiments in hydrogen it must have come from the palladium filaments. Now oxygen and hydrogen in the presence of a red-hot filament would combine to form water-vapour, and if this were frozen out by liquid air, gradually all the oxygen would be removed, hydrogen being present in great excess. So in one experiment the filament was kept red-hot for three hours while liquid air was on the side-tube, so that any oxygen present must have combined with hydrogen to form water-vapour, and have thus been frozen out. But at the end of the three hours, the glow still appeared when the filament was heated more strongly.

In another experiment, new palladium filaments were heated in the evacuated apparatus, and the gas which they gave off was pumped away, so that any oxygen would thus be removed. But on filling the apparatus with hydrogen and passing the discharge with the filaments as cathode to produce carbon monoxide or dioxide, a bright glow was obtained on

heating the filament. Hence oxygen is not necessary for the production of the glow.

Now the Rev.Gill says that if his tube had been filled with hydrogen before being exhausted, then the glow could not be obtained in the ordinary way, i.e. by merely heating the filament: but that the passage of the discharge with the filament as cathode caused the glow to appear. This is to be expected for the necessary carbon monoxide or dioxide is produced by the discharge.

He further states that an excess of hydrogen interferes with the production of the glow. However, an excess of hydrogen in his experiments would mean an excess of water-vapour, since oxygen was present. Hence it would be this excess of water-vapour which tended to prevent the appearance of the glow, and not the excess of hydrogen itself.

Carbon Dioxide.

Several times the apparatus was filled with pure dry carbon dioxide at a pressure of about 1 mm. No glow appeared merely on heating the palladium: but on passing the discharge with the filaments as cathode, the glow quickly appeared. The spectrum of the discharge now contained the bright hydrogen lines H_α and H_β in addition to very bright carbon monoxide bands. On several occasions it was found that the pressure measured after the passage of the discharge was greater than

the pressure before passing the discharge: this would be due partly to the change of carbon dioxide into carbon monoxide and oxygen under the influence of the discharge, and partly to the liberation of hydrogen from the palladium.

As usual, a flask of solid CO_2 on the side-tube removed H_α and H_β from the discharge-spectrum, and caused the glow to fade. Thus the necessary hydrogen had been present only as a constituent of water-vapour, and so was removed by ~~solid~~ solid Co_2. The fact that the necessary gas which is removed is hydrogen is further proved in that, when some hydrogen was admitted to the carbon dioxide, then solid CO_2 had no effect on the glow.

In a mixture of hydrogen and carbon dioxide, a brilliant glow appeared on heating the palladium, without it being necessary to pass the discharge. Hence the glow is not due to some direct action of the discharge; and in the experiments previously described, the function of the discharge has been only to produce one of the necessary gases from the brass leads or the electrodes.

The glow was obtained in mixtures of hydrogen and carbon dioxide at pressures between 2·68 and ·82 mm. Various pressures and proportions of the two gases were tried, and it was found that the brightest and most extensive glow was obtained when the pressure was just over 1 mm., Hydrogen being present a little in excess of the carbon dioxide. The presence

of solid CO_2 on the side-tube of the apparatus had no effect on the glow in these mixtures. This was to be expected because solid CO_2 cannot freeze carbon monoxide or dioxide, and hydrogen was present in a non-condensible form, so that both the necessary gases remained when the solid CO_2 was on.

Carbon Monoxide.

The apparatus was several times filledwith pure dry carbon monoxide to various pressures between ·99 and ·70 mm. There was no glow on heating the palladium, but on passing the electric discharge with the filaments as cathode, H_β appeared in the discharge-spectrum, and a bright glow was obtained. Placing a flask of solid CO_2 on the side-tube of the apparatus had no effect on the glow, showing that hydrogen was not present as a constituent of water-vapour. This might have been expected since the only possible source of oxygen was the palladium filaments.

Some oxygen was introduced into a mixture of hydrogen and carbon monoxide in which a bright glow had been obtained; but it was found that the oxygen did not improve the glow. As some carbon dioxide would be produced in these circumstances, this seems to show that carbon dioxide is not more efficient than carbon monoxide in producing the glow. However palladium is known to occlude oxygen in addition to hydrogen, so possibly a trace of carbon dioxide is present even when only carbon

monoxide is admitted. In order to discover whether the possible small trace of carbon dioxide, due to oxygen from the palladium, is necessary for the glow, new palladium filaments were raised to red-heat in vacuo: the pressure rose to about ·002 mm. This gas was then pumped away and the apparatus was filled with carbon monoxide. On now admitting a little hydrogen a very bright glow was obtained. This shows that it is the hydrogen, and not the oxygen, from the palladium which is needed for the glow; and that carbon monoxide, not carbon dioxide, is required in the production of the glow.

Gill states that palladium which had been heated for some time lost the power to produce the glow: and that even if it were saturated with hydrogen, and were made the electrode in a vacuum-tube discharge, the power of producing the glow was not restored. But it is not certain that carbon monoxide was present in these circumstances, so that the failure to obtain the glow may have been due to the absence of this gas. He also says that the only means of restoring to palladium the power to produce the glow, was to leave it exposed to the air for about six weeks. During this time the palladium may have in some way acquired carbon monoxide in some form, and hence it would produce the glow on being heated.

It was found during the experiments described in this

paper that, if on heating palladium no glow appeared, then on admitting either hydrogen or carbon monoxide, according to which was needed, the glow could always be obtained.

From these experiments with palladium in various mixtures of gases, it was concluded that hydrogen and carbon monoxide are the only gases required in the production of the glow.

Then it was thought that the production of the glow might not be due to a peculiar property of palladium, but merely to the heating of the gases in the neighbourhood of a hot metal filament: so it was decided to see if platinum would give a glow in similar circumstances.

Platinum.

The apparatus was thoroughly cleaned to remove all sputtered palladium: and then two filaments of very thin platinum foil were mounted. All possible mixtures and pressures of the various gases were tried, and the electric discharge was passed for a long time in every mixture. During ten days, experiments were made with the platinum filaments, but no sign of a glow was ever obtained, even in the conditions which ~~have~~ had been shown to be most favourable for the appearance of a glow from palladium. Since the platinum could obviously be raised to a much higher temperature than the palladium, owing to its higher melting-point, the fact that the glow was

not produced with a platinum filament seems to point to the conclusion that the function of the hot palladium was something more fundamental than a mere temperature effect.

If, however, platinum is exposed to the sputtering from palladium, then it gives a good glow on being heated. One platinum and one palladium filament were mounted in the apparatus, which was filled with hydrogen and carbon monoxide at 1·46 mm. pressure. The platinum was raised to white-heat several times, but no glow appeared. Then the electric discharge was passed in both directions for some time: but no glow was obtained from the platinum. Next, the palladium was heated, and immediately a very bright glow appeared. Now on cooling the palladium and heating the platinum, a faint glow appeared. On continued heating, this glow became much fainter showing that as the platinum lost the sputtered palladium, it lost the power to produce the glow. The palladium was heated again, so that more of it sputtered on to the platinum, and now on heating the platinum, a brighter glow appeared: and as the experiments continued, the glow from the platinum became quite bright as more palladium sputtered on to it.

Peculiar Action of Discharge.

In all the mixtures of gases experimented upon, it was found that if a bright glow could be obtained, then after the passage of the discharge with the filaments as anode, only a very faint glow, or perhaps none, was obtained on heating the filament. However, the effect was only temporary, for if the filament were heated again about five minutes after the cessation of the discharge, then the glow appeared as usual. It may have been that one of the necessary gases was driven into the filaments, or into the platinum plate, by the action of the discharge, and that this gas only returned after the discharge had stopped.

Spectrum of Glow.

The spectrum of the glow was observed twice, on each occasion the apparatus containinga mixture of hydrogen and carbon dioxide. When observed by means of a small direct-vision spectroscope, the glow spectrum consisted of a faint continuous background and one bright line in the violet. With a Hilger constant- deviation spectroscope there was seen a faint continuous spectrum stretching from about 5820 to 4816 where there was a dark region: this continuous part was probably there before the glow appeared, and was due to light from the hot filament reflected by the glass walls. When the

glow appeared, a faint blue band was seen, extending from 4407 to 4325 approximately, the setting for the middle of the band being 4375.

Below are given my readings of the glow-spectrum, and also Gill's for comparison.

		Gill's readings.
Beginning of continuous spectrum	5820	6220
" " dark region	4816	4697
Red end of blue band	4407	4419
Middle " " "	4375	4380
Violet end " "	4325	4343

Gill attributes this blue band entirely to carbon monoxide, but gives no explanation for the non-appearance of the other carbon monoxide bands. Now this band may correspond to the carbon monoxide band of which the sharp red end is at 4394, especially as carbon monoxide is undoubtedly necessary for the production of the glow.

It is an established chemical fact that palladium, charged with hydrogen, in the presence of water-vapour causes carbon monoxide and oxygen to combine to form carbon dioxide. Gill explains the production of the glow by supposing it to be due to the occurrence with luminescence of the above reaction. But it has been proved in this paper that oxygen and water-vapour are not necessary for the production of the glow.

Further it has been shown that Gill's failure to obtain the glow in the absence of water-vapour was most probably due to the absence of hydrogen, not of water-vapour itself; and he does not appear to have experimented in the absence of oxygen. Hence it is not possible to accept Gill's explanation of the production of the glow.

The exact explanation of the origin of band spectra is not known, although it is generally thought that they are due to molecules in a disturbed condition, as distinct from atoms in a disturbed condition.

There is very little evidence for the explanation of the origin of the carbon monoxide band spectrum. From an investigation of the spectra of discharges in Geissler tubes filled with carbon monoxide or carbon dioxide, Hulthén[1] concludes that the bands 5610, 5198 and 4835 belong to the same commencement condition of the molecule, while the bands 4835 and 4394 belong to the same end condition.

However, Duffieux[2] from a consideration of the limits of interference obtained from the bands of carbon monoxide, attributes these bands to the free atoms of carbon and oxygen: but he does not mention the band 4394. Since the above evidence is to a certain extent contradictory, it is not

(1). E.Hulthén. Ann. d. Phys. 71. 1923. p.41.

(2). M.Duffieux. Compt. Rend. 175. 1922. p.169.

possible to give an exact explanation of the origin of the band 4594 in the spectrum of the glow.

Now, it has been shown in this paper that only palladium, hydrogen and carbon monoxide are required in the production of the glow. Palladium charged with hydrogen is known to act as a catalyst. Hence it may be that palladium charged with hydrogen produces some disturbance in the condition of the carbon monoxide molecules, possibly without causing ionisation, and that the glow is due to the return of the carbon monoxide to the normal condition.

Action of the Induction Coil Discharge in causing Disappearance of Gas in presence of Cooling Agent.

In the course of the investigation of the circumstances in which the blue glow could be obtained on heating palladium, the effect of cooling a tube attached to the main part of the apparatus, in a vessel of solid CO_2, was frequently tested. In these cases the effectiveness of the cooling agent in removing gases from the apparatus ~~were~~ was tested by passing the induction coil discharge through the remaining gas and examining its spectrum for changes due to the solid CO_2; It was noticed that if the discharge were passed for a few minutes, the character of the luminosity changed, the whiteness changing to deep purple and pink, while the carbon monoxide bands faded from the spectrum. This was first noticed in a mixture of hydrogen and a small amount of carbon monoxide, but it was subsequently found to occur in all the mixtures of gases in which the glow had been obtained. On heating the palladium filament after stopping the discharge, it was found that the glow could no longer be obtained, a fact presumably to be attributed to the disappearance of the oxide of carbon under the influence of the induction coil discharge in the presence of the cooling agent (solid CO_2).

A great deal of research [1] has been carried out on the

(1) Research Staff of the General Electric Company. Phil.Mag. Nov.1920. May.1921. Brodetsky & Hodgson. Phil.Mag. May. 1916. Vegard. Ann.d.Phys. 1916. Soddy & Mackenzie. Proc. Roy. Soc. A. 1908.

action of an electric discharge in causing the disappearance of gas from a vacuum-tube: and many explanations have been put forward to account for the results obtained in the various gases. But a full and certain explanation of all the circumstances has not yet been arrived at. A large part of the work has been carried out, using tungsten and platinum filaments in single gases. The circumstances of the present observation of the phenomenon of the disappearance of gas under the influence of the discharge appeared to differ considerably from any employed in the investigations by other workers, referred to above.

Moreover, the possibility of taking advantage of the appearance or non-appearance of the glow on heating the palladium filament, as an indication of the presence or absence of certain definite gases (hydrogen and oxides of carbon) after passing the discharge in different circumstances introduced a new feature into this type of investigation, and further experiments were therefore carried out to investigate the action of the discharge in the presence of a cooling agent. Some account of the results of this investigation is given below.

Experimental Results.

A glow was obtained in hydrogen by passing the electric discharge so that carbon monoxide was produced. Then Solid CO_2

was placed on the side-tube of the apparatus: since both hydrogen and carbon monoxide are present in a non-condensible condition, the glow could still be obtained. The electric discharge was passed: gradually the appearance of the discharge changed from a whitish to a deep purplish colour, and the carbon monoxide bands faded from the spectrum. Then, on heating the filament, no glow could be obtained. However, when the solid CO_2 was removed and the side-tube allowed to warm up, a bright glow could again be obtained, and it remained when the solid CO_2 was replaced on the side-tube.

In all the gases and mixtures, it was impossible to obtain the glow after passing the discharge while solid CO_2 was on the side-tube. But generally, e.g. in a mixture of hydrogen and carbon monoxide, only a very faint glow returned on the removal of the solid CO_2. Further, whether or not the replacing of the solid CO_2 caused the glow to fade again depended upon the gas present: e.g. in hydrogen the glow remained when the solid CO_2 was replaced, but in carbon monoxide, the glow faded. This suggested that the discharge had changed the condition of one of the necessary gases into a form condensible by solid CO_2.

Now it was found that the passage of the discharge while solid CO_2 was on the side-tube, caused a decrease of pressure in the apparatus; e.g. in one case, the pressure decreased from .92 to .68 mm. Hence at least one of the gases necessary

for the glow must have been removed from the apparatus by this action. So, when only a faint glow returned on the removal of the solid CO_2 after the passage of the discharge, it was decided to test if the admission of one or other of the necessary gases could restore the glow. In a mixture of hydrogen and carbon monoxide, the discharge was passed with solid CO_2 on the side-tube, and the glow could no longer be obtained. On removing the solid CO_2 only a faint glow returned. Carbon monoxide was then admitted, and the glow was then bright, and remained so when the solid CO_2 was replaced. The discharge was again passed, and the glow disappeared. On removing the solid CO_2, no glow could be obtained. Some carbon monoxide was admitted, but still no glow could be obtained. When, however, some hydrogen was admitted, then a bright glow appeared on heating the filament. This showed that both hydrogen and carbon monoxide were removed in some degree, one being completely removed, and the gas which was entirely removed seemed to depend on which gas had been present in excess.

Next it was decided to condense a considerable pressure of gas by the passage of the discharge with solid CO_2 on the side-tube, and then to experiment in this gas.

The apparatus was filled with hydrogen and carbon monoxide in about equal proportions, and solid CO_2 was placed on the side-tube. On heating the palladium a very bright glow was

obtained. Then the discharge was passed: gradually the whiteness of the discharge disappeared, and it became purplish, while the carbon monoxide bands faded from the spectrum. Now, on heating the palladium, no glow appeared. The apparatus was opened to the pressure-gauge, and the pressure was found to have decreased by about ·1 or ·2 mm. Some of the original mixture of hydrogen and carbon monoxide had remained in the pressure-gauge, so that on opening the apparatus, some of this gas entered it, and now a bright glow appeared on heating the filament. The discharge was again passed and its appearance changed as above. When the glow could not be obtained, the pressure was again found to have decreased, and the entry of more gas again gave a bright glow. So the discharge was passed repeatedly in both directions, and more and more gas was admitted. That both gases were disappearing was shown in that sometimes carbon monoxide was needed, and sometimes hydrogen, to restore the bright glow. Finally when about 1·5 mm. pressure of gas had disappeared, the solid CO_2 having remained on the side-tube all the time, then the residue of gas was quickly pumped away to a pressure of about ·002 mm. It seems probable that this small amount of gas was hydrogen or carbon monoxide according as hydrogen or carbon monoxide had been in excess before pumping out the gas: but it was found that the results obtained when hydrogen had been in excess did not differ from those obtained when carbon monoxide had been in excess. Then the apparatus being shut off from the gauge, the

solid CO_2 was removed from the side-tube. White patches were seen on the inside of the tube, but these gradually disappeared as the tube warmed up. It was left for some time to allow all the condensed gas to evaporate. In order to discover if the gas was still in a condition to be condensed, the solid CO_2 was replaced. After some time the apparatus was opened to the pressure-gauge. But the rise of pressure was inappreciable, e.g. from ·0033 to ·0051 mm, so that almost all of the gas had been re-condensed. Again the solid CO_2 was removed, and the side-tube allowed to warm up. Then the palladium was heated. At first there was no sign of any glow, but after heating the filaments many times, a faint glow appeared. To test whether the hot filament had restored any of the gas to a non-condensible condition, the solid CO_2 was replaced. In ten minutes, no glow could be obtained. The apparatus was then opened to the pressure-gauge, and there was found to be a small, but definite, increase in pressure, e.g. from ·0051 to ·104 mm. Hence the hot palladium had changed some gas from a condensible into a non-condensible form. But either hydrogen or carbon monoxide, or both, was still in a condensible form, since the glow could not be obtained with solid CO_2 on the side-tube.

With a view to discovering which gas was missing, some carbon monoxide was introduced, solid CO_2 being on the side-tube: but the glow still could not be obtained. Hence hydrogen must have been missing. It was thought that the discharge might

have the power to restore the hydrogen, so the solid CO_2 was removed, and the discharge was passed with the filaments as anode. Then the solid CO_2 was replaced, and now the glow did appear on heating the palladium. Hence the action of the discharge must have been to restore the hydrogen. Moreover, even if no additional carbon monoxide had been admitted before passing the discharge, then after the passage of the discharge with the filaments as anode, solid CO_2 no longer removed the glow, so that both gases necessary for the glow were present. Hence both constituents are in a non-condensible form after the passage of the discharge. It was shown above that the discharge was necessary to restore the hydrogen to this form, but it is not known whether the carbon monoxide was in a suitable form before the passage of the discharge. Therefore to see whether the discharge had restored the carbon monoxide, another experiment was made in the gas which evaporated after being condensed out under the influence of the discharge when the side-tube was cooled. After obtaining a faint glow by heating the palladium this glow was removed, as usual, by replacing the solid CO_2 : then hydrogen was admitted, and the glow could now be obtained with solid CO_2 still on the side-tube. Therefore the discharge was not necessary to restore the carbon monoxide to a non-condensible form: but this conversion must have been brought about by the heating of the palladium.

Later, gas from a mixture of hydrogen and carbon monoxide was condensed out by solid CO_2 under the influence of the electric discharge as described above, there now being one platinum and one palladium filament mounted in the apparatus. The final residue of gas having been pumped away to a pressure of about ·002 mm., the solid CO_2 was removed to allow the condensed substances to evaporate, and then it was replaced. As above, the increase of pressure was inappreciable: so the solid CO_2 was again removed and the filaments were heated. It was found that it was not necessary to heat the platinum filament for so long a time as it had been necessary to heat the palladium filaments before the glow appeared. This was probably due to the fact that the higher temperature of the platinum would more quickly bring about the necessary change in the condition of some of the gas.

As before, on now replacing the solid CO_2, the glow could not be obtained, though a pressure of ·06 mm. remained, showing that the hot filament had changed some of the gas into a non-condensible form, but that at least one of the necessary gases was still absent.

It had been found in the case with ~~the~~ two palladium filaments, that the passage of the discharge with the filaments as anode restored the hydrogen: so it was decided to seeif the discharge would have a similar effect in this case, there being one platinum and one palladium filament. Hence, after

obtaining a faint glow by heating the filaments in the gas, which had been condensed out under the influence of the discharge, and after finding that solid CO_2 caused this glow to fade, then the discharge was passed with the filaments as anode, no solid CO_2 being on the side-tube. H_β was quite bright in the discharge spectrum. Then on replacing the solid CO_2, no glow could be obtained so that one at least of the necessary gases was still in a condensible form. The reverse discharge was then passed, the solid CO_2 having been removed: the carbon monoxide bands were faint in the discharge-spectrum and undoubtedly carbon monoxide was produced by the discharge. After this, placing solid CO_2 on the side-tube only made the glow fainter, it could not entirely remove it. So the necessary hydrogen had been restored by the passage of the discharge with the filaments as anode, but the carbon monoxide had still been in a condensible condition, even after heating the filaments and passing the discharge in the first direction.

In another experiment the filaments were heated in the gas which had evaporated after having been condensed out under the influence of the discharge with solid CO_2 on the side-tube, and a faint glow was obtained. With a view to discovering if either of the necessary gases had been restored to a non-condensible form by the heating of the filaments, it was decided to introduce each of these gases in turn to the evaporated gas.

So, instead of passing the discharge, some hydrogen was admitted. Solid CO_2 still removed the glow. This supports the conclusion reached above that carbon monoxide must still have been in a condensible condition. This behaviour is contrary to that with two palladium filaments. After this, ~~this~~ the discharge was passed with the filaments as cathode; as above, its appearance whitened, and the carbon monoxide bands appeared brightly in the spectrum. Now placing solid CO_2 on the side-tube only made the glow fainter, but could not entirely remove it: this was to be expected since both hydrogen and carbon monoxide were now present in non-condensible form.

Then in another experiment, some carbon monoxide was admitted to the gas which had evaporated, after having been condensed out under the influence of the discharge when the side-tube was cooled. Solid CO_2 could still remove the glow. Hence hydrogen as well as carbon monoxide was not in a suitable form. On now passing the discharge with the filaments as anode, the glow could be obtained with solid CO_2 on the side-tube, so that the discharge had restored the hydrogen, as had been the case when both filaments were palladium.

Discussion of Above Results.

In the experiments just described, some of the results when both filaments are palladium differ from those when one filament is platinum and one is palladium.

In both cases, after having condensed out some gases by the passage of the discharge in the presence of the cooling agent, these gases were allowed to evaporate by removing the solid CO_2. These gases (hereafter called the evaporated gases) are not in a suitable condition for giving the glow. Heating the filaments for a sufficiently long time restores some of the gas to a suitable condition, but at least one of the necessary constituents is left in a condensible form, as evidenced by the fact that the replacing of the solid CO_2 removes the glow.

When both filaments are palladium, only the hydrogen is missing when solid CO_2 is replaced on the side-tube, since admitting hydrogen, after the treatment outlined above, enables the glow to be obtained even with solid CO_2 on the side-tube. A similar state of affairs is reached, if instead of admitting hydrogen, the discharge is passed with the filaments as anode before replacing the solid CO_2.

Now it has been found[1] that many gases can be made to adhere to glass under the influence of the electric discharge: the amount adhering depends on the gas and on the state of the glass, e.g. whether it is cooled, or not. Further, this adhesion is not due primarily to chemical reaction, although such reaction may aid adhesion by producing a gas which adheres more easily than that originally present. In general, most of

(1). General Electric Company's Research Staff. Phil.Mag. May. 1921.

of the gas which has disappeared owing to adhesion can be restored by heating the glass vessel: but it has been found that part of the gas cannot be restored by heating the glass, but only by the passage of a discharge. This action of the discharge is probably due to the bombardment of the glass by charged particles.

Hence, the above suggested action of the discharge in restoring the hydrogen would be the liberation , by the discharge, of the hydrogen from the glass walls.

When one filament is platinum and one is palladium, hydrogen is not the only constituent which remains in a form condensible by solid CO_2 after heating the filament in the evaporated gases. This is proved by the fact that steps have ~~been~~ to be taken to produce both carbon monoxide and hydrogen before the position is such that a glow can be obtained even on replacing the solid CO_2 on the side-tube.

Since there is a palladium filament present in both cases, the difference in the results obtained in the two cases must be attributed to the presence of the platinum filament in the second case. There are two possible explanations of the difference. Either the gas, that evaporates when the solid CO_2 is removed from the side-tube after the passage of the discharge, is the same in both cases, but the action of the hot filament

is different in the two cases: or there is a difference in the two cases in the manner of disappearance of the gases under the influence of the discharge when the side-tube is cooled.

On the following consideration, the first alternative can be ruled out. In both cases, a palladium filament was heated in the evaporated gases; and yet the results obtained from the subsequent treatment were different in the two cases. Thus the difference could not have been merely due to a different action of the hot filament in the two cases.

Hence it seems that the second alternative must be the explanation. Since in both cases a glow could be obtained by heating in the evaporated gases, this glow being however removed by solid CO_2, the carbon monoxide and hydrogen must have entered into chemical combinations to form substances condensible by solid CO_2, although one substance can be used instead of carbon monoxide in the production of the glow.

It was found that different steps have to be taken, in the two cases, to restore carbon monoxide so that a glow can be obtained with solid CO_2 on the side-tube; hence carbon monoxide must have been removed under the influence of the discharge in a different manner in the two cases, in addition to the removal by the formation of a condensible substance, as mentioned above.

When both filaments are palladium, the other means of

disappearance of carbon monoxide may be by adhesion of this gas, or of carbon dioxide, to the glass walls under the influence of the discharge when the side-tube is cooled. Since replacing the solid CO_2 caused the re-condensation of nearly all the evaporated gases, as shown by pressure measurements, the gas which has disappeared by adhesion is not restored in any degree merely by warming the cooled side-tube. However, if hydrogen was admitted to the evaporated gases, then after very little heating of the filament, a glow was obtained which would remain when the solid CO_2 was replaced. Hence the heating of the filament must have restored some of the carbon monoxide which had adhered. That a little heating of the filament restores carbon monoxide while much more heating is necessary to restore some of the hydrogen to a form suitable for the production of the glow, is shown in that considerable heating of the filament is needed to obtain a glow in the evaporated gases, unless hydrogen has been admitted. But the hydrogen, restored by heating the filament, is still in a form condensible by solid CO_2, probably water-vapour, since the glow cannot be obtained when the solid CO_2 is replaced.

When one filament was platinum and one was palladium, none of the carbon monoxide was restored by heating the filaments to a form non-condensible by solid CO_2: so that none of the carbon monoxide can have disappeared by adhesion to the glass walls, as was supposed to have occurred when both

filaments were palladium. This reaction would only fail to occur if the carbon monoxide were being used in some other reaction, connected with the presence of the platinum. It has been found (1) that the disappearance of some of the gas during the passage of an electric discharge is connected with the sputtering of the cathode. So in the second case, the disappearance of some of the carbon monoxide may have been due to the binding of the gas by sputtered platinum, this reaction occurring to the exclusion of the adhesion suggested above in the case when both filaments were palladium. Further it has been found in the previous experiments, that the carbon monoxide, which has been removed by the sputtering of the platinum, is not restored by the removal of the solid CO_2 from the side-tube, nor by the heating of the filaments: but there is no reason for expecting that it would thereby be restored.

Some of the gas produced by considerable heating of the filaments in the evaporated gases is incondensible by solid CO_2, as shown by the small pressure remaining when the solid CO_2 was replaced. But this gas is unnecessary for the production of the glow since steps have ~~been~~ to be taken to produce both carbon monoxide and hydrogen before a glow can be obtained when solid CO_2 is on the side-tube, in the case with one platinum and one

(1). Vegard. Ann.d.Phys.1916. Brodetsky & Hodgson. Phil. Mag. xxxi. 1916.

palladium filament. Further, in the case when both filaments were palladium, the amount of gas, non-condensible by solid CO_2, which was produced by heating the filaments in the evaporated gases, was actually larger than in the other case: this extra amount of gas would probably be due to the carbon monoxide which had been restored, by the heating of the palladium, after having adhered to the glass walls.

Now it has been suggested that considerable heating of the filaments is necessary to restore some hydrogen to a form suitable for the production of the glow, although still condensible by solid CO_2: and it may be that during this change, the non-condensible gas, which is unnecessary for the production of the glow, is also produced. Hydrogen and carbon monoxide were the only gases originally present, and it seems unlikely that this non-condensible gas could be a compound of hydrogen and carbon; and it cannot be carbon dioxide since carbon dioxide is suitable for use in the production of the glow. It might possibly be oxygen which has been set free as the final result of a series of complicated reactions: or it might be due to traces of various gases which the discharge had probably liberated from the walls.

The action of the discharge in causing both absorption and liberation of various gases is still an uncertain matter, and investigators have very often found that they were unable

completely to account for their results.

An attempt has here been made to account for the results observed in a general way. It is concluded that in the presence of palladium, and in the presence of platinum and palladium, both hydrogen and carbon monoxide are caused to disappear by the passage of an electric discharge when solid CO_2 is on the side-tube. In both cases some of the gases probably disappear through undergoing chemical combinations to form substances condensible by solid CO_2. When both filaments are palladium, some of the carbon monoxide seems to disappear by adhesion to the glass walls, while when a platinum filament is employed, the sputtered platinum may in some way remove some carbon monoxide.

General Summary.

In the first part of the paper it has been shown that a blue glow is obtained on heating a palladium filament in the presence of certain gases at low pressures, the only necessary gases, however, being hydrogen and carbon monoxide. It is suggested that palladium charged with hydrogen produces a disturbance of the carbon monoxide molecules, and that the glow is produced by the return of the molecules to the normal condition.

In the second part of the paper, an investigation was

made of the disappearance of hydrogen and carbon monoxide, from a mixture of these gases, under the influence of the induction coil discharge in the presence of a cooling agent (solid CO_2). An attempt has been made to determine the manner of disappearance of these gases. It is suggested that both gases disappear as a result of having entered into chemical combinations which produce substances condensible by solid CO_2; and that, in addition, carbon monoxide may disappear by adhesion to the glass walls, or its disappearance may be in some way connected with the sputtering of the metal cathode. The actual circumstances of the experiment determine which of the two latter means of disappearance causes some of the carbon monoxide to disappear.