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XXX.—On the Occlusion of Hydrogen by Copper.

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In the Chemical Society's Journal (1876, 1, 178) the results of some experiments of mine on this subject are briefly recorded. I then arrived at the conclusion that rolled copper wire, when oxidised at the blowpipe and subsequently reduced in hydrogen at a red heat and allowed to cool in the gas, occluded hydrogen to the amount of from 0063 to $\cdot 0077$ gram of hydrogen for 100 grams of copper; the hydro-

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gen being weighed as water, which was produced by igniting the charged metal in a current of dry air, and absorbed by a V-tube containing pumice moistened with strong sulphuric acid.

I was induced to return to this subject by the appearance of a paper by Dr. Thudichum (published in the Chemical Society's Journal for 1876, 2, 251), in which he gives the results of some experiments, by himself and Dr. Hake, showing that mere traces of hydrogen are occluded by freshly reduced copper, and that no appreciable error could be caused in organic analysis by the oxidation of such minute quantities of occluded gas.

The results of a number of careful experiments have led me to adhere to the belief that the occlusion of hydrogen by copper may be, and probably often is, the cause of serious error on the side of excess in the determination of hydrogen in the ultimate analysis of nitrogenous organic substances.

Dr. Thudichum has pointed out the great discrepancies which exist between various chemists, and even between the analyses of the same chemist, as regards the actual quantity of hydrogen occluded by copper. I will simply append the list given by him, with the addition of his own name and that of a German chemist, O. Lietzenmayer, who has recently attacked this subject in the *Deut. Chem. Ges. Ber.*, 11, 306-309.

Weight	of coppe	er.		Source.	Hy	drogen oc	cluded.
$\uparrow 100$	grams	Oxide	••••			.0006	(Graham)
J	,,	Wire				·0003	(Graham)
J	,,	New v	vire			.0006	(Thudichum)
L	,,	Wire	re-oxidis	ed and	re-reduced	•0001	(Thudichum)
	,,	Oxide				.0029	(Melsens)
	,,	"				.0200	(Melsens)
	,,	Wire g	gauze			·0061	(Lietzenmeyer)
	,,	Rolled	wire	• • • • • • •		$\cdot 0074$	(Johnson)

The experiments of Graham and Thudichum, whose results I have accordingly bracketed together, were performed on an entirely different principle from the rest, and cannot therefore be fairly compared with those which follow. Even allowing, however, for the fact that the first four numbers were obtained by removing the occluded hydrogen with Sprengel's pump at a red heat and measuring it over mercury, whilst the last four were obtained by weighing it as water after oxidising it at a red heat in a current of dry air, there is still sufficient discrepancy between the results of experiments conducted upon similar principles to demand a careful examination into its cause. This discrepancy I hope to account for satisfactorily by the results of the following experiments; but I will first point out two facts which are noticeable in the above table: first, the amount of hydrogen found is far greater in the second set of experiments than in the first; and secondly, the second method of experimentation is obviously the one which is best suited for settling the question at issue, viz., how far the occlusion of hydrogen by copper may influence the accuracy of results obtained in organic analysis, inasmuch as the occluded hydrogen is sure to meet with sufficient oxygen, in most analyses at all events, to convert it entirely into water.

The first set of experiments, then, was undertaken with a view to place beyond doubt the answer to the question, whether copper does or does not occlude sufficient hydrogen to introduce a serious error in organic analysis. The experiments were conducted upon the same principle as before, viz., the copper was oxidised at the blowpipe, reduced in hydrogen, allowed to cool in that gas,* and the metal was then re-oxidised in a current of dry air, the water produced being collected in a counterpoised V-tube containing pumice moistened with strong sulphuric acid. Further precautions were, however, taken to avoid the presence of extraneous moisture, atmospheric or otherwise, in the counterpoised drying-tube. For this purpose the air or oxygen in which the charged copper was oxidised was in all cases dried, not only by solid caustic potash and strong sulphuric acid, but also, and finally, by passing through a V-tube containing phosphoric anhydride. Any error due to moisture contained in corks was also avoided, the front of each combustion-tube being drawn out and connected with the weighed pumice-tube by india-rubber tubing. In every experiment the dry air or oxygen was drawn through the cold apparatus till the pumice-tube had constant weight, after which heat was at once applied to the copper without in any way disturbing the connections.

Occlusion of Hydrogen by Copper in different states.

The first conclusion arrived at was as follows:—When metallic copper is repeatedly oxidised and reduced by hydrogen in the same tube progressively decreasing quantities of hydrogen are occluded till a minimum (apparently constant) quantity is reached. Thus 47.6 grams of rolled copper wire yielded the following weights of water in a series of oxidations in the same tube, each oxidation being of course followed by reduction:—

Experiment	I	0.006	gram.
- ,,	II	0.0055	,, ,,
	III <i>.</i>	0.006	,,
	IV	0.0045	
,,	V	0.0045	,,

* The hydrogen was displaced from the tube by dry air.

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Experime	ent I	0.010	gram.
,,	II	0.0103	,,
,,	III	0.0085	,,
,,	IV	0.004	,,
,,	$\mathbf{v} \dots$	0.004	,,

It was conclusively proved in the above experiments that the purity of the hydrogen employed for reduction did not in any way influence the result as regards the quantity of that gas occluded by the copper. Hydrogen passed through solution of silver nitrate, and completely dried by P_2O_5 , produced results apparently identical with that which had simply passed through one bottle containing strong sulphuric acid. It would appear from the following experiment that the amount of oxide on the surface of the copper at the time of its reduction in hydrogen materially influences the subsequent occlusion.

18.8 grams of rolled copper-wire never ignited in air or oxygen, and presenting a clean metallic surface, was reduced in hydrogen at a red heat and cooled in the gas. After intense ignition in dry air for half an hour only 0.0013 gram of water had been collected, whereas the same copper, after being strongly ignited at the blowpipe and again reduced in hydrogen, yielded 0.0045 gram of water.

Again, the same 37 grams of copper which were used in previous experiments and yielded when last oxidised after reduction only 0.004 gram of water, having been strongly ignited in the blowpipe and again reduced, furnished 0.0115 gram of water at a red heat in air.

It appears, then, that the pulverulent metal resulting from reduction of *oxide* on the surface of the copper is the most active agent in occluding hydrogen, and the progressively decreasing amount of gas taken up may readily be accounted for by the *condensation* which this metallic powder undergoes when heated strongly in hydrogen gas, the final result being that much dense metal is produced and less surface is consequently offered for absorption.

These deductions receive further confirmation from the following experiments:---

 $16\cdot1$ grams of pulverulent copper, obtained by reducing $20\cdot2$ grams of copper oxide (prepared by igniting carbonate of copper) in hydrogen at a red heat and allowing the reduced metal to cool in that gas, yielded $0\cdot032$ gram of water when oxidised in a current of dry air. This is equivalent to $\cdot020$ gram of hydrogen for 100 grams of copper.

Even the finely-divided metal resulting from reduced oxide, however, undergoes such condensation by repeated reductions in hydrogen that its occluding power is finally almost lost. This is clearly proved by these two observations :---

(1.) 18.3 grams of copper, obtained from the same source as that employed in the above experiments, viz., by ignition of cupric carbonate, but which had been frequently oxidised and reduced, was once more oxidised by strong ignition in the blowpipe and then reduced in hydrogen at a red heat and allowed to cool in the gas. Only .0035 gram of water was obtained on heating the reduced metal to redness in a current of dry pure air.

(2.) 16.6 grams of copper, from the same source and subjected to the same treatment as the above in every way, yielded only 0.009 gram of water in one experiment and 0.0055 gram H_2O in a second experiment, when oxidised in air, after reduction in hydrogen.

But it was noticed that in the above experiments that a potash-bulb placed between the pumice-tube (for absorption of water) and the aspirator underwent an increase in weight each time the copper was ignited in air, and that not only in the case of reduced oxide, but also when rolled copper wire was made use of. The contents of the potash-bulb (which had been filled with pure potash) were found on analysis to consist not of potassic carbonate, but *potassic sulphate*; and as the weight of the bulbs was quite constant when dry air was passed through the apparatus in the cold, this sulphuric acid was accounted for by oxidation of sulphur contained in the copper. A possible source of error, leading to an exaggeration of the weight of hydrogen really occluded by the copper, was here detected, viz., the retention of SO_3 -vapour by the sulphuric acid contained in the pumice-tube, leading to an increase in its weight not due to water produced by oxidation of occluded hydrogen.

With a view to determine the *absolute weight* of hydrogen occluded by copper under very favourable circumstances, and at the same time to ascertain if possible how far the error above-mentioned might have affected the accuracy of previous results, the following experiment was executed :---

72.3 grams of copper oxide, intended for organic analysis, was strongly ignited before the blowpipe, reduced in a current of hydrogen in a combustion-tube at as low a temperature as possible, and allowed to cool in the gas. The finely-divided copper thus obtained (after displacement of the hydrogen by dry air) was now heated to redness in dry air, the resulting vapours and gases being drawn by an aspirator through—

(1.) A counterpoise V-tube containing phosphoric anhydride.

(2.) A counterpoise set of bulbs containing pure solution of potash.

(3.) A counterpoise V-tube containing pumice moistened with sulphuric acid.

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The P_2O_5 -tube increased 0.184 gram. Large drops of water were visible during the early stages of the process. The oxide employed was equivalent to 57.74 grams of metallic copper, so that the weight of hydrogen occluded was in the proportion of 0.035 gram to 100 grams of copper. Inasmuch as a portion of P_2O_5 was converted into a paste by the moisture produced, it is quite possible that some SO_3 may have been retained and added to the weight of water in this experiment, but it is probable that the error thus produced is slight, for the potash-bulb, which was placed beyond the drying tube, underwent an increase of 0.023 gram, which agrees nearly with the results obtained in former experiments. Since the potash-bulb was provided with a small drying tube, the pumice and H_2SO_4 -tube beyond underwent no change in weight.

Now as the weight of the above apparatus was unchanged in its various parts by the passage of dry air through it for one hour, there is no source of SO_3 or SO_2 in the form of gas, except the metallic copper in the combustion-tube (which must have been contaminated with sulphur).

The contents of the potash-bulb after the experiment were found to be free from nitrite, *i.e.*, when acidulated with dilute sulphuric acid, the liquid produced no blue colour in a solution of starch and iodide of potassium, but abundance of *sulphate* was found.

It appears from the above results that the sulphur contained in metallic copper undergoes conversion into SO_3 when the metal is oxidised in dry air. Both the copper carbonate and the oxide of copper for organic analysis showed contamination with S by $Ba(NO_3)_2$ added to their solution in HNO_3 .

The following experiments, in which granulated copper was employed, illustrate the influence of surface upon the weight of hydrogen occluded on the one hand and that of repeated oxidation and reduction in diminishing the occlusive power on the other :---

36.4 grams of granulated copper, after being roasted in air and subsequently reduced in hydrogen, yielded 0.0838 gram of water when oxidised in dry air. This is equivalent to 0.0255 gram of hydrogen to 100 grams of copper.

Again, 46 grams of the same copper similarly treated gave 0.0995 gram of water.

The same copper, after four reductions, occluded hydrogen equivalent to 0.027 gram of water, or only one-third of the original weight.

The above experiments seem to establish beyond all doubt the fact that commercial copper does occlude hydrogen, sometimes in considerable quantities, and apparently always in sufficient quantity to produce a serious error in organic analysis. They also account quite satisfactorily for the discrepancies observed between the occlusive power assigned by various chemists to the metal.

The following experiments, however, show that physical condition, or extent of *surface* offered by the metal, is not a sufficient explanation of the wide differences observed between the weights of water or hydrogen obtained from equal weights of reduced metal in the experiments I have just described.

It occurred to me that the copper obtained by reduction of precipitated oxide at a very low temperature, as in the experiments of Dr. Wright (*Chem. Soc. Jour.*, p. 13 of this volume), would be in an extremely advantageous form for occluding large quantities of hydrogen. Accordingly I precipitated a boiling solution of pure sulphate of copper with some hot solution of pure caustic potash, and washed the precipitate by decantation with boiling water almost daily for some weeks, till at last, not only were the washings free from sulphuric acid, but some of the oxide, when dissolved in pure nitric acid, gave no precipitate with solution of baric nitrate after standing for 48 hours.

I found that this pure precipitated oxide of copper, after being dried in a tube at 110° in a current of dry air, gave rather more than the calculated quantity of water when reduced in dry hydrogen at 110° . I subsequently discovered that this was due to incomplete drying of the oxide at 110° . The oxide is not *entirely* reduced in pure dry hydrogen at 110° , and either the unreduced oxide or the freshly reduced metal retains some *water* at 110° , which it parts with at a higher temperature, but not a trace of hydrogen is occluded. These facts are established by the following experiments :—

(1.) 3.792 grams of copper obtained by reducing pure precipitated CuO in pure dry hydrogen at 110° was heated to redness in dry hydrogen, a counterpoised V-tube, containing pumice moistened with sulphuric acid having been adjusted. After cooling in the hydrogen the copper had lost 0.025 gram in weight, whilst the pumice-tube had gained 0.030 gram, or more than would be accounted for by oxygen in the copper.

To ascertain whether hydrogen escaped unoxidised when the copper was heated to redness in air—

(2.) Dry air was passed through a tube containing 3.65 grams of Cu reduced at 110° (from same source as above) and then through a tube containing dry CuO, finally through a counterpoised pumice and sulphuric acid tube. The copper oxide was first ignited strongly, then the reduced copper, dry air passing all the time; the pumice-tube increased 0.010 gram in weight.

Hence 3.65 grams Cu evolved 0.01 gram H₂O at red heat in air.

It is clear that the water collected from the copper ignited in dry

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air must either be due to retained moisture or to the oxidation of occluded hydrogen, whilst the water obtained from the same copper when ignited in hydrogen must be assigned to the same cause, or to the reduction of CuO unacted upon at 110°, but speedily attacked at a red heat in hydrogen gas. Suppose the reduction at 110° to be complete and hydrogen gas to be occluded by the reduced copper, it is evident that the hydrogenised metal will lose weight when heated to redness in hydrogen without any formation of water; or, if it be capable of retaining occluded hydrogen at a red heat, its weight will remain constant, provided that it has retained no moisture at 110°. If it has retained moisture, but occluded no hydrogen, the loss it will sustain will be equal to the gain of a drying tube placed in front; whilst, if the reduction at 110° is incomplete and moisture has been retained as well, the gain by such a drying tube will be much in excess of the loss of weight by the copper, and the latter was actually observed in the above experiments. Thus 3.792 grams of copper reduced from precipitated Cu at 110° yielded 0.03 gram of water collected in the drying tube, whilst it lost 0.025 gram in weight. This experiment, then, clearly proves that no hydrogen was occluded by the copper at 110°, for, had the copper retained hydrogen, it would have lost weight either equal to that gained by the drying tube or in excess of that quantity.*

If 3.65 grams lose 0.01 gram H_2O , 3.792 grams would lose .0104 gram H_2O .

Hence 0.0146 gram out of the 0.025 gram lost by 3.792 grams of Cu reduced at 110°, when heated to redness in dry hydrogen, would be due to oxygen retained by the copper at 110° in hydrogen, whilst 0.0196 gram of the water collected and weighed would be due to the product of combination of that retained oxygen with hydrogen at a red heat; and the theoretical quantity so produced would be 0.0163 gram. It is obvious that had hydrogen been occluded at 110°, which was evolved in hydrogen at a red heat, the loss by the copper in the above experiment would have been in excess of the gain by the pumice-tube, whereas the reverse was actually observed. Hence water, not hydrogen, is evolved in hydrogen at a red heat by copper reduced at 110° in hydrogen.

(3.) It was proved that the same copper, after being subjected to a red heat in hydrogen and cooled in the gas, had not occluded hydrogen even at that temperature; for, when it was oxidised in dry air at a red heat, a pumice-tube placed in front had a perfectly constant weight.

(4.) Even if the pure precipitated oxide of copper be strongly

* The hypothesis that reduced spongy copper may contain occluded hydrogen in presence of unreduced copper oxide is not here discussed, since the existence of such a phenomenon cannot be proved by the method of experimentation employed.

heated in air before being reduced in hydrogen, the spongy metal, whether the reduction be at a high or low temperature, appears to occlude none of the gas.

Thus, then, the most finely divided metal conceivable does not occlude any hydrogen, which clearly proves that some other influence governs the occlusion of hydrogen by copper, besides the mere state of subdivision in which the metal happens to be at the time when it is reduced in the gas.

Remembering the interesting results obtained by Prof. Gladstone and Mr. Tribe (Chem. Soc. Jour., 33, 308) upon the reducing action of hydrogenised copper on potassium chlorate, &c., I reduced some common copper oxide (intended for organic analysis) in hydrogen in the usual way, washed it with boiling water till the washings gave no precipitate with silver nitrate solution. After boiling this reduced pulverulent metal with some pure potassium chlorate for half an hour abundance of *chloride* was detected in the supernatant liquid. On the contrary, the pulverulent metal, obtained by reduction of precipitated copper oxide at 110° in hydrogen, produced no chloride after boiling for one hour with the same potassium chlorate. Thus finely divided copper itself appears to be without action upon a boiling aqueous solution of potassium chlorate, whilst the conclusion that this form of the metal does not occlude hydrogen receives confirmation from the above experiments. Moreover, the reduction of potassic chlorate by hydrogenised commercial copper was proved to be due to its occluded hydrogen, and not to couple-action of metallic impurities, by the following experiment :---

Some of the commercial (impure) copper oxide employed in the above experiment was reduced in hydrogen in the usual way. It was then divided into two equal portions, one of which was simply freed from its contained chlorides by washing, whilst the other was first ignited in pure nitrogen, allowed to cool in that gas and then washed with water. The two portions of pulverulent copper thus prepared were now boiled with equal volumes of the same solution of pure potassic chlorate. The supernatant liquors being tested with solution of silver nitrate, that above the hydrogenised copper showed evidence of reduction of its chlorate by the precipitate of silver chloride which it yielded, whilst that which had been boiled over the copper freed from occluded hydrogen by ignition in nitrogen yielded no precipitate with silver nitrate solution.

Behaviour of Hydrogenised Copper in different Gases.

Having now definitely answered the question whether commercial copper recently reduced in hydrogen occludes that gas, my attention

was next directed towards offering some explanation of the vast discrepancy between the results obtained by chemists who heat the charged copper in a current of dry air and those produced by the method of heating to redness in a vacuum and measuring the gas evolved by the Sprengel pump. The explanation which naturally uggested itself was, that the charged copper refuses to part with its occluded hydrogen at a red heat in a vacuum. Accordingly I made some experiments with a view to ascertain whether the hydrogenised copper would retain its occluded gas when heated to redness in a current of gases which have no oxidising action at high temperatures. The first gas tried was carbonic anhydride. It soon became manifest, however, that this gas was quite unsuited for the purpose; for in several experiments quite ponderable quantities of water were evolved by recently reduced copper when heated to redness in a current of dry \dot{CO}_2 . Thus, 27 grams of copper yielded in one experiment 0.009 gram H₂O; in another, 0.013 gram; in another, 0.011 gram. The only possible explanation of these results being that the hydrogen was oxidised by the CO₂ at the temperature of the Hofmann's furnace, the following experiments were undertaken, in order to ascertain whether this reaction was dependent upon the presence of a metallic surface, or whether it would take place when the two gases were simply subjected to a high temperature in presence of some indifferent body.

By means of a T-shaped tube, a stream of mixed carbonic anhydride and hydrogen gases was passed through the following purifying apparatus: -(1.) A solution of sodic bicarbonate. (2.) A solution of silver nitrate. (3.) Two pumice-tubes containing strong sulphuric acid, and (4.) A U-tube containing phosphoric anhydride. The purified gases were next conducted through a combustion-tube filled with fragments of broken porcelain, and finally through a tube containing pumice and sulphuric acid. The weight of this last tube was taken when filled with hydrogen; and this gas was always passed in the cold till the counterpoised tube had a constant weight after one hour before each experiment. The apparatus being thus proved to be in thorough working order, the mixed gases (CO₂ and H) were conducted through the combustion-tube together, the temperature being kept at red heat for a given time, after which the supply of carbonic anhydride was stopped and the dry hydrogen passed alone for some time; the pumice-tube was then again weighed full of hydrogen, the increase giving of course the weight of water produced during the application of heat :---

In Exper	iment I,	0.047	gram	of H_2O	was produced	in $1\frac{3}{4}$	hou	rs.
;,	11,	0.030		,,	"	1	· ,,	,
. ,,	III,	0.060		,,	,,	,,	,,	,
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These results were considered to prove satisfactorily that hydrogen is slowly oxidised by CO_3 at the highest temperatures of the combustion (Hofmann's) furnace. The gases were not *drawn* through by an aspirator, but were *driven* through from behind by the pressure produced in gas generators.*

The next gas employed was carbonic oxide. Even when the utmost precautions were taken to purify this gas, small quantities of water appeared to be produced during ignition of the hydrogenised copper therein, and this even when an alkaline pyrogallate was employed to remove traces of oxygen. Thus 46 grams of granulated copper when ignited in the dry pure gas yielded 0.008 gram H_2O , or at least there was so much increase in the weight of a counterpoised pumice and H₂SO₄-tube, whose weight had been constant for one hour whilst the CO was passed in the cold. The same copper, however, after being cooled in the CO, was ignited strongly in a current of pure dry air and vielded only 0.001 gram of water; whilst, after being again reduced in dry hydrogen, cooled in that gas and ignited in dry air only, it yielded 0.027 gram of water. Hence the copper cannot retain its occluded hydrogen in a current of carbonic oxide gas; for the occlusive power of the copper in the above experiments was proved to be equivalent to 0.027 gram of water, whilst only 0.009 gram H₂O was produced from it by alternate ignition in CO and dry air; therefore two-thirds of its occluded hydrogen must have escaped unoxidised during the ignition in carbonic oxide.

The same result was obtained by employing *nitrogen* carefully purified. No water could be obtained by igniting in dry air copper which had been heated to redness in pure nitrogen, and allowed to cool in that gas, after being previously charged with hydrogen.

It appears, then, that hydrogenised copper cannot retain its occluded gas when ignited in a current of carbonic oxide or nitrogen.

I now repeated the experiments of Graham and Thudichum, and obtained precisely similar results. Mere traces of hydrogen were collected (in most experiments) by the Sprengel pump.

The retention of hydrogen by freshly reduced pulverulent copper heated to redness in a vacuum is proved by the following experiment:--

 $35\cdot3$ grams of powdered oxide which had been made into a paste with nitric acid, *fused* and then powdered in a mortar, were reduced in pure dry hydrogen and allowed to cool in the same gas. The tube containing the freshly reduced metal was now exhausted by Sprengel's pump, and its temperature raised to the full red heat of a Hofmann's

* Reduction of CO₂ by H at a red heat: vide *Watts' Dict.*, article "Marsh-gas;" item Lowthian Bell, "Chemical Phenomena of Iron-Smelting," pp. 122-126.

Reduction of CO by II at a red heat : vide I. L. Bell, loc. cit., p. 131.

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furnace. The tube having remained vacuous and collapsed for one hour, no measurable gas was collected. The copper, having cooled in the vacuous tube, was now introduced into a dry combustion-tube and ignited in carefully dried air, when 0.062 gram of water was collected and weighed.

In a similarly conducted experiment, 23.47 grams of copper oxide yielded 0.037 gram of water after reduction in hydrogen, ignition in a vacuum, and final oxidation in dry air.

The fact that hydrogenised copper parts with its occluded hydrogen when ignited in a current of nitrogen gas, was made use of to afford corroborative evidence that the *hydrogen* and not simply *water* is occluded by copper reduced from its oxide by that gas.

Samples of commercial copper oxide were reduced in hydrogen as in previous experiments at different temperatures, and afterwards ignited in dry pure nitrogen gas, carefully freed from oxygen, the gases issuing from the combustion-tube being conducted through (1) a counterpoised sulphuric acid tube, (2) a tube containing ignited oxide of copper, and (3) a second counterpoised sulphuric acid apparatus. It was found that when the reduction of the metal had been effected at temperatures below 700°, water was always evolved, and caused an appreciable increase in the weight of the first drying bulb; whilst the second drying tube also showed evidences of hydrogen occluded as such in the copper, evolved in the nitrogen and oxidised by the ignited copper oxide. On the other hand, when the temperature of reduction was increased to a red heat, and when the hydrogen was passed at that temperature till no ponderable water was evolved, the first drying tube retained a constant weight during the ignition of the copper in nitrogen, whilst the second tube appreciably increased in weight, visible drops of moisture being often observed in front of the red-hot copper-oxide tube.

A very probable explanation of the discrepancy between results obtained by Drs. Thudichum and Hake and my own, has been offered by my friend Dr. C. R. A. Wright (to whom I am also indebted for several other valuable suggestions), viz., that some of the occluded hydrogen may be oxidised by unreduced *suboxide of copper*, retained in the deeper strata of the metal, such oxidised hydrogen, of course, escaping detection by the process of Sprengelising the hydrogenised copper. And this explanation is rendered additionally probable by the observation that copper reduced at *low temperatures* yields *water* as well as hydrogen when ignited in a stream of pure nitrogen; for it is at least as plausible an explanation of this fact to assert that some suboxide of copper which escaped reduction at that low temperature, became reduced by a portion of the occluded hydrogen evolved at the higher temperature of the ignition in nitrogen with production of

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water, as to say that this water had been occluded in the metal as such.

The practical result, however, arrived at by the above experiments is sufficiently obvious, viz., that it is unsafe to employ copper freshly reduced in hydrogen for the reduction of oxides of nitrogen in organic analysis, unless the metal be previously ignited in nitrogen gas.