

The difference between the above results and those of Lang may be due in part to the greater fineness of our particles, but it is more probably explained by the fact that Lang permitted the evolved hydrogen sulfide to escape, thus constantly displacing the equilibrium, whereas in these experiments all the flasks were carefully stoppered.

The action is due, apparently, to a solution of the red sulfide in the acid, followed by a reprecipitation of the less soluble black modification. These black crystals under the microscope showed the characteristic orthorhombic faces of the mineral stibnite.

Further experiments were made to determine the effect of temperature on the velocity of transformation. A 20% hydrochloric acid solution was used, with the same proportions of acid and red sulfide as before. The experiments were carried out in a thermostat at a series of temperatures up to 75° with a maximum variation of 0.5°; 25cm. test-tubes were used instead of flasks.

Temperature. °C.	Time required.	
	Hrs.	Min.
26.5	44	..
30	29	..
35	16	..
40	9	..
68.5	..	62
75	..	32

The very rapid increase of speed of transformation with rise of temperature is noteworthy.

Under similar conditions, a 20% solution of hydrobromic acid gave no visible blackening, even after 20 hours at 75°.

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## THE REDUCTION OF COPPER OXIDE BY HYDROGEN.

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This investigation of the reduction of copper oxide by hydrogen was undertaken in the hope that the results might throw some light on the mechanism of the catalytic combination of hydrogen and oxygen in the presence of metallic copper, in a study of which we have been engaged.<sup>1</sup> Since copper oxide may be reduced by hydrogen and the resulting copper may be re-oxidized without difficulty at temperatures at which the metal is catalytically active, it would appear that, in all probability, the catalytic reaction proceeded as a result of the alternate oxidation and reduction of the copper. Certain of our results were apparently inconsistent

<sup>1</sup> The results of this investigation will be published shortly.

with this interpretation, however, and it was thought that a study of the reduction reaction by itself might be of assistance in clearing up the discrepancy. As an examination of the literature revealed that this reaction possessed several peculiarities of its own, the investigation seemed the more worth while.

A rather extensive investigation of the reduction of copper oxide by hydrogen has been carried out by Wright, Luff and Rennie.<sup>2</sup> Hydrogen was passed at a constant rate through a U-tube containing copper oxide held at various fixed temperatures by means of vapor baths and the rate of reduction determined by weighing the U-tube from time to time. It was found that the reduction was preceded by an "incubation" period, the length of which was greater the lower the temperature. Following the incubation period, (during which there was no perceptible reaction) reduction set in at a steadily increasing rate (induction period) till a maximum was reached, after which the rate decreased gradually to zero as the reaction approached completion. Experiments were carried out at several temperatures between 130° and 257°. In other experiments, copper oxide was spread on the bottom of a small flask heated in a vapor bath, and a current of hydrogen was passed through the flask. The authors' description of the progress of the reaction is instructive. "The reduction commenced visibly by the formation of a red speck amongst the little mass of copper oxide at the lowest part of the bulb; this quickly spread, becoming rapidly larger and larger until practically the whole mass became a reddish metallic powder, the progress of the reaction reminding one of the slow deflagration of a quantity of touch paper, *the reducing action being apparently propagated from particle to particle through the mass.*" This occurred, be it remembered, in the presence of an excess of hydrogen.

It is evident from these results that the reaction is auto-catalytic, copper being the auto-catalyst, in all probability. The reaction starts only after some time—at least as evidenced by the change in weight of the tube containing the oxide<sup>3</sup>—with the formation of one or more visible nuclei of copper. From these as centers, the zone of reaction, that is, the copper-copper oxide interface, spreads out and as its area increases the rate of water formation increases.

If the induction period is due to the initial absence of metallic copper, it should be possible to shorten it or cause it to disappear altogether by adding already reduced copper to the oxide about to be reduced. It seemed

<sup>2</sup> Wright, Luff and Rennie, *J. Chem. Soc.*, 33, 1 (1878); 35, 475 (1879).

<sup>3</sup> That the tube does not lose weight during the first part of the run does not necessarily prove that reaction is not taking place at an exceedingly slow though steadily increasing rate. Various sources of error, particularly the retention of the water formed through adsorption, might obliterate any effect of the expected magnitude. The reproducibility of the results would indicate that the reaction does not start merely by accident.

worth while to try to confirm this experimentally. Further, since water as well as copper is a product of the reaction, it was decided to determine the effect of adding more water to the system as moisture in the hydrogen.

### Experimental.

A sketch of our apparatus is shown in Figure 1.

Electrolytic hydrogen from the tank A was passed through heated palladized asbestos in the tube B to convert the small percentage of oxygen present in the hydrogen to water, through the flow-meter C, the phosphorus pentoxide drying-tube D and then through the electrically heated furnace E, which contained the copper oxide. The

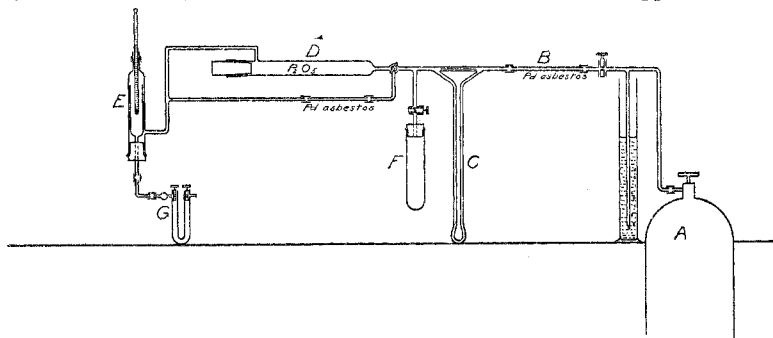


Fig. 1.—Apparatus.

furnace consisted of two concentric glass tubes, the inner one of which contained the oxide. The outer tube was wound with Nichrome wire and was covered with magnesia pipe covering. Rates of reduction were measured by determining the rates of water formation. This was accomplished by passing the effluent hydrogen through a U-tube containing calcium chloride (G) for definite time intervals and noting the increase in weight due to water absorbed. The rate of reduction is expressed throughout in terms of milligrams of water absorbed by the calcium chloride tube in 5 minutes' passage of the effluent hydrogen. The rate of flow of the hydrogen was maintained constant at 50 cc. per minute. Samples of 5 cc. apparent volume of copper oxide, weighing within a few tenths of 10 g. were always employed. As the containing tube was 2.5 sq. cm. in cross section, this gave a layer of copper oxide about 2 cm. deep. An imported copper oxide in granules intended for organic analysis, "hirsekorngrösse," (about 10- to 20-mesh) was used.

For the purpose of checking the results of Wright, Luff and Rennie as to the character of the reaction and in order that we might have standards with which to compare our other experiments, we have obtained reduction curves at 150° and 200°. These are presented in Fig. 2. It will be seen that these possess the characteristics reported by the above authors. There is the incubation period (practically non-existent at 200°) followed by the period of increasing rate of reduction to a maximum and finally the period of decreasing rate. At 200° the maximum rate of reduction corresponded to the formation of 130 mg. of water in 5 minutes. If all the hydrogen had been consumed the rate of formation of water would have been 184 mg. in 5 minutes. Although the design of the furnace

prevented direct visual observations of the progress of the reaction, its characteristics were made clear by an examination of samples in various stages of reduction. It was found that reduction *practically never started at the top*, where the preheated hydrogen first met the charge, but usually at some point near the middle of the charge along the side of the tube. From these points as nuclei, the reaction zone appeared to spread over the whole mass.

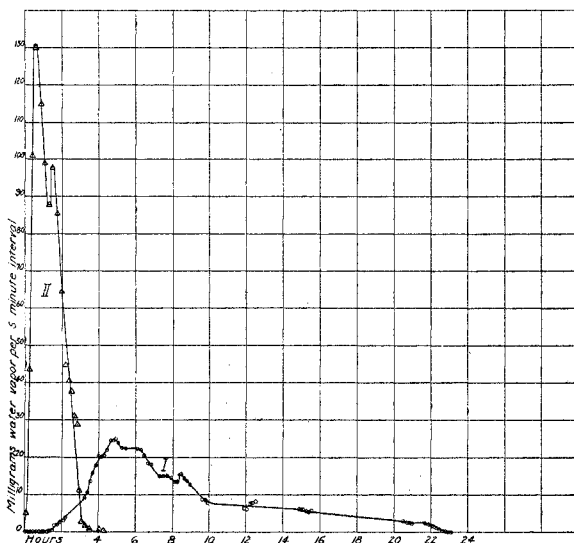


Fig. 2.—Reduction of copper oxide by hydrogen. Curve I, reduction at 150°. Curve II, reduction at 200°.

**Effect of Copper.**—In one experiment, a layer of previously reduced granules was placed on top of the oxide, which was then treated with hydrogen at 150°. The result is shown graphically by Curve II, Fig. 3. Curve I represents the standard reduction with pure copper oxide and hydrogen. It is the initial portion of Curve I, Fig. 2 on a larger scale. By comparing the curves it may be seen that the layer of copper considerably hastened the setting-in of the reaction and nearly eliminated the incubation period. An examination of the sample after reduction had proceeded for several hours showed that the reaction had begun at the top of the charge in contact with the copper and had proceeded downward in wave front roughly normal to the direction of hydrogen flow. Since ordinarily reduction begins within the charge rather than at its surface, the top being reduced toward the end instead of at the beginning of the run, it would appear that the layer of copper had rendered the oxide in contact with it the more reactive, substantiating the assumption that the reaction is autocatalytic and takes place mainly and most easily at a copper-copper

oxide interface. The reaction did not subsequently reach as high a rate as did the standard, as the curve shows. Ordinarily, the reaction starting at some point within the charge, the area of the interface will be at least twice the cross-sectional area of the tube since there will be an interface above and another below the reduced portion. In the case described above the area of the interface was only that of the cross-section of the tube, and, as it is thought that the rate of water formation is proportional to the interface area, the reaction would not be expected to reach as high rates as it did in the standard run, since the interface area is only about half as great.

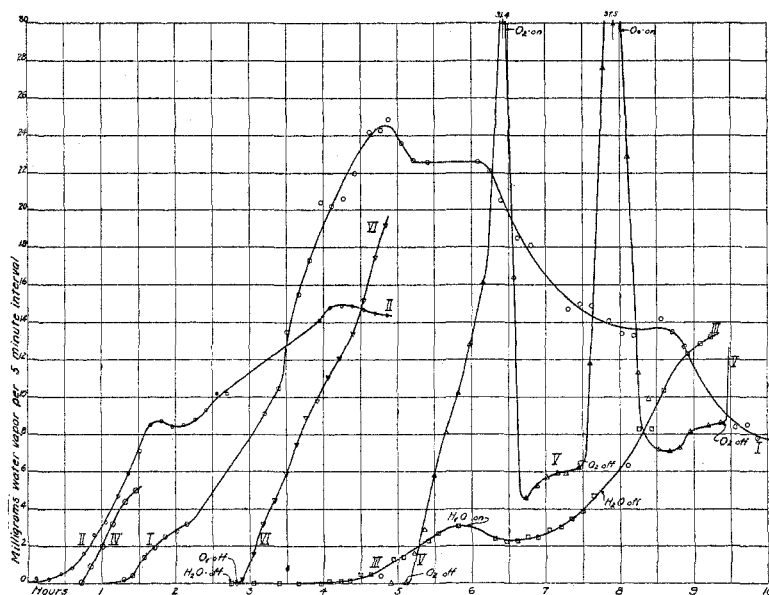


Fig. 3.—Reduction at 150°. Curve I, Normal reduction. Curve II, in presence of metallic copper. Curve III, effect of water vapor; 5 mg. per 5-minute interval. Curve IV, effect of preliminary treatment with dry air. Curve V, effect of oxygen equivalent to 10 mg. of water per 5-minute interval. Curve VI, effect of oxygen equivalent to 5 mg. of water per 5-minute interval.

**Effect of Water Vapor.**—Water vapor was added to the hydrogen in the following manner.—An electrolytic gas generator F (Fig. 1), consisting of a wide mouth test-tube containing caustic soda solution in which were immersed 2 spiral nickel wire electrodes, was connected to the hydrogen line. By connecting the electrodes of the generator in series with a variable resistance and a milliammeter, electrolytic gas could be generated at a definite rate into the hydrogen stream, and, by causing the latter subsequently to pass over heated palladized asbestos, the electrolytic gas could be reconverted into water vapor. In these experiments, the cell was

run at such a rate that 5 mg. of water was decomposed (and subsequently synthesized over the palladized asbestos) in 5 minutes. The milliammeter setting was 0.180 amperes. In the 250 cc. of hydrogen which was passed in 5 minutes, this is equivalent to about 2.7% water vapor by volume. This amounts practically to saturation at room temperature. The result of passing this saturated hydrogen over copper oxide at 150° is shown by Curve III, Fig. 3. Not only was reduction prevented during the exposure (reduction would normally have started in 1 to 1½ hours) but in addition did not start for nearly 2 hours after the electrolytic gas was shut off and pure dry hydrogen alone passed over the oxide.

From these results it is clear that water vapor strongly inhibits the initial reaction between hydrogen and copper oxide—that is, it effectively prevents, at this temperature, the formation of copper nuclei. Since it is a product of the reaction it clearly has no such powerful action on the subsequent reaction at the interface. This was confirmed by adding water vapor to the hydrogen again some time after reaction had started. Referring again to Curve III, Fig. 3, it is seen that under these conditions, after an apparent temporary set-back, the reaction proceeded in much the normal fashion.

That the system experienced an exceptionally long incubation period even after the water vapor was shut off suggested that possibly adsorbed water was partially responsible for this phenomenon in the ordinary runs, especially since water vapor so strongly inhibits the preliminary reaction. Accordingly, the effect was tried of drawing dry air through the charge at 150° for 3 hours prior to reduction in order to sweep out any moisture. Air dried by means of a calcium chloride tower was aspirated through the sample at the rate of 50 cc. per minute. At the end of 3 hours, the sample was cooled nearly to room temperature, the air then displaced by hydrogen and the temperature again raised to 150°. The reduction proceeded according to Curve IV, Fig. 3. The result was that the incubation period was reduced to about half its normal length but was not completely wiped out. It would appear, therefore, that the presence of adsorbed water is not alone responsible for the incubation period.

According to Wright, Luff and Rennie,<sup>2</sup> when air (probably undried) was drawn over heated copper oxide for 15 minutes and then the hydrogen current substituted, the incubation period was considerably lengthened. We believe this to be due to the fact that moist air was used and the air swept out by hydrogen while the oxide was hot, when a small quantity of water would certainly be formed, the water absorbed from the air and that formed by catalytic combination being sufficient to retard the reaction.

At 200°, the effect of water vapor was to cause a definite though brief incubation period when none was normally noted. (Curve II, Fig. 4. Curve I refers to the normal reduction.) It did not prevent the reaction

starting, as it did at  $150^{\circ}$ , however. After having once started, the reaction proceeded normally, as was to be expected if water vapor does not affect the reaction at the copper-copper oxide interface.

**Effect of Oxygen.**—Results obtained during the experiments on the catalytic combination of hydrogen and oxygen in the presence of copper indicated that the oxygen present inhibited the reduction of the oxide formed simultaneously with the water, for when the oxygen was shut off, the rate of water formation always rose temporarily to a value considerably greater than that when oxygen had been present.

Further evidence that oxygen inhibits the reduction of copper oxide by hydrogen is afforded by some experiments of Bone and Wheeler.<sup>4</sup> Using a method involving circulation of the gases in a closed system, one part of which was a heated tube containing copper oxide, they found that the rate of consumption of hydrogen from a mixture of 2 parts of hydrogen and 1 part of nitrogen was nearly 10 times as great as from electrolytic gas (2 parts of hydrogen and 1 part of oxygen). The experiments were carried out at  $214^{\circ}$ . It can hardly be assumed that the nitrogen accelerated the reaction; rather would it appear that, with electrolytic gas, the oxygen present inhibits the reduction to such an extent that the combined

rates of reduction and hydrogen-oxygen combination are less than the normal rate of reduction in the absence of oxygen.

For the purpose of confirming these indications, the rates of reduction of copper by hydrogen containing oxygen were determined. Oxygen was added to the hydrogen by connecting with the hydrogen line the electrolytic gas generator used in the experiments with water vapor. The oxygen concentrations are expressed in terms of the corresponding weight

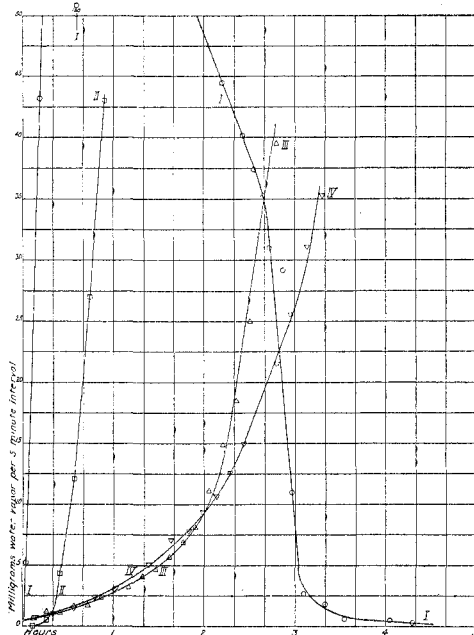


Fig. 4.—Reduction at  $200^{\circ}$ . Curve I, normal reduction. Curve II, effect of water vapor: 5 mg. per 5-minute interval. Curve III, effect of oxygen equivalent to 5 mg. per 5-minute interval. Curve IV, effect of oxygen equivalent to 10 mg. per 5-minute interval.

<sup>4</sup> Bone and Wheeler, *Phil. Trans.*, 206A, 1 (1906).

of water in milligrams which could theoretically be formed from the oxygen during a 5-minute passage of the mixture. Thus, "oxygen equivalent to 10 mg. of water per 5-minute interval" means that the quantity of oxygen present in the hydrogen passed through the apparatus in 5 minutes was sufficient to form 10 mg. of water. This is equivalent to 2.5% of oxygen by volume at 25°, the hydrogen being run at the rate of 50 cc. per minute.

As had been anticipated, it was found that the presence of oxygen very seriously interfered with the reduction reaction. In one experiment, hydrogen containing oxygen equivalent to 10 mg. of water per 5-minute interval was passed over copper oxide for 5 hours, during which period no formation of water could be detected. It appears, therefore, that under these conditions the oxide is not appreciably reduced nor does it possess appreciable catalytic activity toward the combination of hydrogen and oxygen. (Curve V, Fig. 3.) Normally, with pure hydrogen, reduction would have become measurable in 1 to 1½ hours. Directly the oxygen was cut off, reduction set in, the maximum rate being much greater than in any other runs. The incubation period was therefore eliminated by this treatment. It will be recalled that similar treatment with water vapor only resulted in postponing the incubation period. After reduction had been allowed to proceed for a short time, oxygen was again turned on. As a result, the rate of reduction was very markedly repressed, dropping from 31 to 5 mg. of water per 5-minute interval, and did not recover until the oxygen was shut off. Subsequent addition of oxygen resulted in a repetition of this effect.

As Curve VI, Fig. 3, shows, oxygen equivalent to 5 mg. of water per 5-minute interval produces similar effects.

At 200°, (Curves III and IV, Fig. 4), the effect of oxygen was to retard the reduction very strongly though the latter was not completely prevented. The quantities of water formed under these conditions are undoubtedly due in part to catalytic combination; nevertheless, it is clear from the curve that at the end of 3 hours, the charge had not been appreciably reduced whereas reduction would normally have been nearly complete at the end of this time.

The effects produced by oxygen are seen to be quite distinct from those produced by water vapor. (It was possible that they might have been due to the formation of the latter.) At 150°, preliminary treatment with hydrogen containing water vapor not only results in no water formation but postpones the incubation period till the water vapor is cut off. After reduction has commenced, however, further addition of water vapor has no marked effect. With oxygen in the hydrogen, on the other hand, the incubation period is eliminated (that is to say, reaction starts directly the oxygen is cut off) although no reduction takes place during the exposure; but addition of oxygen after reduction has started very markedly represses



the reaction. Clearly water vapor is only effective in the initial reaction between hydrogen and copper oxide. This may be attributed to the strong adsorption of water vapor by copper oxide. Comparisons of the quantities of water added to the hydrogen and quantities recovered from the effluent hydrogen during the first few minutes of the exposures to water vapor indicated that quite large quantities of water vapor must have been taken up. Oxygen, on the other hand, probably is effective only in the reaction taking place at the interface. At first sight it would appear that it also inhibits the initial reaction. However, the fact that reduction commenced directly the oxygen was cut off seems to indicate that the formation of copper nuclei had been going on during this period; that is to say, the elimination of the incubation period is taken to indicate that the primary reaction had taken place even in the presence of oxygen. The abnormally rapid rise to an abnormally high maximum after the oxygen had been turned off and reduction once started further indicates the existence at that time of numerous centers of activity. This is consistent with the observations of Dr. A. F. Benton in this laboratory that oxygen is not markedly adsorbed by copper oxide, at these temperatures.

It has been suggested that the retarding effect of oxygen on the reaction at the interface is due to its adsorption by the interface. It is a little difficult to conceive of oxygen remaining long in the adsorbed state at the interface, the seat of activity in the reduction reaction. Granting that oxygen may be so adsorbed, it would seem very probable that it would either immediately be converted to oxide or else react directly with hydrogen to form water (and such a view of the catalytic reaction has its advantages). The reaction to form oxide, if carried far enough, would eventually decrease the area of the interface materially and hence the rate of water formation. Thus, qualitatively, the effect of oxygen would be accounted for. However, the effect of the oxygen is immediate and it is doubtful whether sufficient oxygen is initially present to reduce the interface area by the required amount. This would certainly require all the oxygen present in the gas for a considerable time and yet it is known that even starting with a pure copper surface, the major part of the oxygen goes to form water, although the remainder does combine to form oxide. It is perhaps more satisfactory to assume for the present that oxygen is in fact strongly adsorbed by the interface and protects it from the hydrogen, and although constantly being consumed in the formation of water and oxide, is nevertheless renewed at a sufficiently rapid rate to maintain the protective film.

### Summary.

1. An investigation of the characteristics of the reduction of copper oxide by hydrogen and the effect on the reaction of adding metallic copper

to the oxide and water vapor and oxygen to the hydrogen has been carried out.

2. It has been pointed out that the reaction is auto-catalytic, copper being the auto-catalyst. The reaction thus appears to take place at the copper-copper oxide interface. This is shown by the character of the reduction curve and the fact that addition of metallic copper accelerates the reaction.

3. It has been shown that the presence of water vapor in the hydrogen markedly interferes with the formation of the original copper nuclei from which the reaction zone, that is, the copper-copper oxide interface spreads out; it does not markedly affect the subsequent reaction at the interface, however.

4. The presence of oxygen in the hydrogen strongly inhibits the reaction at the interface but in all probability has no marked effect on the primary reaction, that is, the formation of the original copper nuclei.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF NEW YORK UNIVERSITY.]

## THE HEATS OF SOLUTION AND OF TRANSFORMATION OF THE ACIDO AND AQUO COBALT PENTAMMINES.

BY ARTHUR B. LAMB AND JOHN P. SIMMONS.\*

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### Introduction.

The spontaneous transformations of a number of the acido cobalt pentammines into their corresponding aquo compounds have been carefully studied.<sup>1</sup> They have been found to go nearly to completion at ordinary temperatures in aqueous solutions and, as regards velocity, to follow the course of a monomolecular reaction. At higher temperatures the reaction becomes more evidently reversible, and it has been shown that an equilibrium is attained which strikingly resembles the dissociation equilibria of strong electrolytes in water.

Particularly because of this wider bearing of the subject we have investigated the heat changes accompanying a number of these transformations in aqueous solution. These heat changes could be calculated from equilibria data at different temperatures, did such exist, but unfortunately there are experimental difficulties in studying these equilibria except within a narrow temperature interval. We have therefore been

\* This paper is largely based on a dissertation of the same title submitted by J. P. Simmons in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University, 1912.

<sup>1</sup> Lamb and Marden, *THIS JOURNAL*, **33**, 1873 (1911).