105. *The Reduction of Copper Oxide by Hydrogen.*

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Much of the previous work on the reduction of copper oxide has been carried out by a flow method at atmospheric pressure. Wright, Luff, and Rennie (J., 1878, **33**, 540; 1879, **35**, 475) stated that the reduction by hydrogen between 130° and 257° was preceded by an "incubation" period, the duration of which was longer the lower the temperature. The incubation was followed by an "induction" period, reduction of the oxide setting in at a steadily increasing rate until a maximum was reached, after which the rate gradually decreased to zero as complete reduction was approached. The reduction would therefore appear to be autocatalytic, the copper produced being the autocatalyst.

From somewhat similar investigations, Pease and Taylor (*J. Amer. Chem. Soc.*, 1922, **44**, 2179) concluded that reduction occurred at the metal–oxide interface. During the induction period the action was slow because few such interfaces were developed. The zone of action spread out from these nuclei, and as its area increased, the rate of water formation became greater until a maximum was attained. These workers suggested that the incubation period was in part due to *adsorbed* water, since they were able to reduce the time to about half by drying the copper oxide in a current of air drawn through calcium chloride towers, prior to the introduction of dry hydrogen.

St. John (*J. Physical Chem.*, 1929, **33**, 1438) gave 140° as the lowest temperature at which reduction occurs, though Benton and Emmett had previously obtained positive results in experiments carried out at 106° (*J. Amer. Chem. Soc.*, 1924, **46**, 2728). By careful drying of the reactants, these workers were not able to confirm the period of incubation.

Other methods of studying the above reaction are described by Palmer (*Proc. Roy. Soc.*, 1923, **103**, *A*, 444), who investigated its velocity, and by Taylor and Starkweather (*J. Amer. Chem. Soc.*, 1930, **52**, 2314).

EXPERIMENTAL.

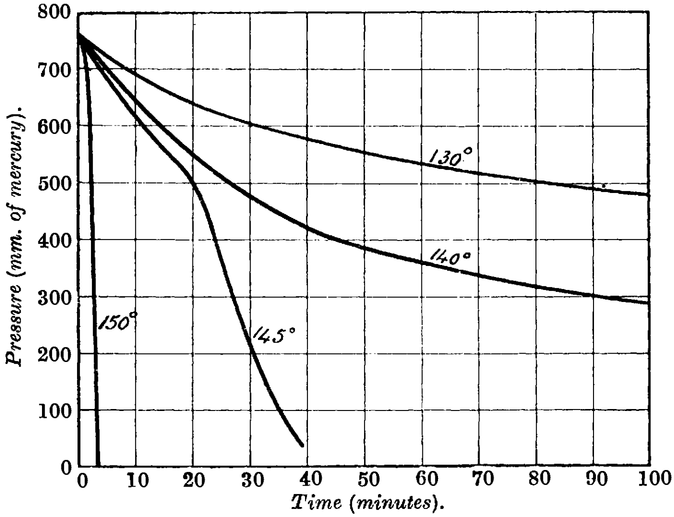
The experiments consisted in heating the oxide with hydrogen in glass bulbs of 125 c.c. or 225 c.c. capacity, at the required constant temperature. The reaction could be stopped after a suitable interval by immersing the bulb in cold water, and the extent of reduction was measured by the fall in pressure in a mercury manometer attached to the bulb, which was then placed in a water-bath at 20°. These reaction bulbs were thoroughly cleansed and dried before an experiment, and a weighed amount of copper oxide was added, which had been previously heated at 105° for some time. The bulbs were evacuated, and filled to the required pressure with hydrogen dried by passing through tubes of calcium chloride and phosphoric oxide. By such means, pressure–time changes were studied at various temperatures with an accuracy sufficient to justify the deductions drawn.

Variations in the Samples of Copper Oxide.—The ease of reduction varied with the sample of copper oxide, and also with the history of a particular specimen. It is known that precipitated or amorphous copper oxide is the most readily reduced by hydrogen. When this is strongly ignited for some time, it becomes more resistant to the action of hydrogen, thereby necessitating a considerably higher temperature for reduction. On the other hand, a carefully prepared and well washed specimen of precipitated oxide is improved by gentle ignition especially in a vacuum. Samples prepared from the metal are extremely resistant to reduction, and so is the oxide obtained by the decomposition of copper nitrate. For example, an extremely active copper oxide obtained by precipitation was reduced to the metal by heating in hydrogen, and then reoxidised in air. The resulting oxide was comparatively inactive and could only be reduced by hydrogen at a considerably higher temperature than that used for the original precipitate. Erratic results may be obtained even with the same sample of oxide, owing to variations in the time and temperature of drying, and the conditions of evacuation of the bulb. A well-dried oxide always gave better results than a moist sample, and maximum reductions resulted if the bulbs containing the oxide were evacuated at temperatures somewhat higher than 120° for a considerable period.

In the following experiments an excess of precipitated copper oxide was enclosed in the bulbs so that the weight could be regarded as being practically unchanged, and by maintaining the conditions of a run of experiments constant, it was possible to obtain reproducible results and useful comparative data.

Incubation and Induction Periods.—In these closed tests with precipitated copper oxide there was no evidence for such periods : if they exist, they must be of short duration. Between 100° and 140°, reduction commenced immediately and with maximum velocity. Then followed a steady fall in the rate, as measured by the fall in hydrogen pressure at given intervals. Typical results are to be seen in the curves in Fig. 1, which have been drawn from the data obtained in a large number of experiments made under identical conditions.

FIG. 1.



The rate of fall of hydrogen pressure is not proportional to the pressure at any instant, but by plotting $\log p/(p - c)$ against t (where c is a constant and t the time), straight lines were obtained for the lower temperatures. This is in accordance with the work of Palmer (*vide supra*) whose equation may be written

$$dp/dt + kp - k_1p^2 = 0.$$

In this equation there is a retarding factor in the speed of reduction, attributed by him to the water vapour pressure which increases with time.

In order to reduce this factor as far as possible, experiments were made at 140° with various initial hydrogen pressures and 4 g. of copper oxide (dried in a vacuum at 130°) in 125-c.c. bulbs, the time of heating being 10 minutes in each case. The results below indicate that the relative falls in pressure (p_0/p) are approximately constant for the initial stage of reduction.

Original press. (p_0, mm.)	610	485	392	250	213	150
Pressure after 10 mins. (p) ...	495	400	325	210	180	124

It would appear that when the mass of copper oxide is large, and if the water vapour could be removed as it is produced, the reaction would be of the first order in accordance with the equation $-dp/dt = kp$. There is, however, another factor which is discussed later, *viz.*, the film of moisture adsorbed on the surface of the copper oxide.

Slow and Rapid Reduction.—The temperature coefficient of the reactions is high, and at much higher temperatures self-heating is to be expected, with a resultant increased speed of reduction. For instance, in an experiment with the bath temperature at 145°, a thermometer embedded in the oxide rose to 147°, and the corresponding pressure–time curve in Fig. 1 confirms this acceleration. Above 150° the evolution of heat was so great that the oxide burst into a glow at some point on the surface from which the flame spread over an increasing area, all the hydrogen being consumed in less than 2 mins. The phenomenon is comparable with the oxidation of readily combustible materials in which slow combustion passes at the ignition point into rapid combustion with flame. The lowest temperature at which " rapid reduction " of precipitated copper oxide was observed was 148°, the initial gas pressure being 1 atmosphere, but with oxides prepared by oxidation of the metal or from copper nitrate the temperature is much higher.

Lowest Temperature of Reduction.—The temperature coefficient of the reaction is sufficiently high between 130° and 140° to suggest measurable chemical action below 106° (compare above), but the rate at 100° (consumption of $<1\%$ of the hydrogen in 1 hr.) was much slower than that calculated (*i.e.*, 3%) : $2\frac{1}{2}$ hours' heating was necessary to obtain a 3% lowering of pressure, and after 15 hours only 13·5% of hydrogen had been removed, the rate of reduction then being extremely slow. Moreover, if the time be sufficiently long, the possibility of reduction at room temperature cannot be excluded, but with copper oxide (dried in a vacuum) and hydrogen there was a small initial reduction of pressure measured at 20°, after which there was no appreciable change on several months' standing.

Action of Moisture.—It is therefore suggested that although copper oxide might be reducible at room temperature, yet if one starts with a pure copper oxide surface the resultant water from the initial reduction is adsorbed on the rest of the oxide surface, producing a protective film that inhibits further attack. This film is so firmly attached that it may be of the nature of a physicochemical complex $CuO{-}H_2O$, the action being reversible, *i.e.*, the compound is dissociated by heat and its formation promoted by increased concentration of water vapour. Comparatively high temperatures are therefore required during reduction in order to decompose this complex, and by the diffusion or sweeping away of the water molecules, a fresh surface is brought into contact with the hydrogen molecules. This will account for the fact observed above, *viz.*, that, as the reduction proceeds in an enclosed vessel, the speed falls off rapidly with increasing partial pressure of water vapour, and also for the fact that the deliberate inclusion of water vapour in the reaction bulbs greatly retards the initial reduction. Moreover such a complex may be decomposed not only by heat but by strong dehydrating agents, and if the above theory is valid, it should be possible to obtain copper from copper oxide at room temperature.

Action of Dehydrating Agents.—The reduction of copper oxide at room temperature proceeds with measurable velocity if it is in contact with dehydrating agents such as calcium chloride or phosphoric oxide, the latter being particularly active. The experiments were carried out in glass bulbs. The phosphoric oxide was first quickly introduced and the copper oxide added so as to cover its surface. The bulb was then filled with hydrogen and attached to a manometer. At first, the rise of mercury was extremely slow, but the speed gradually increased to a maximum and then declined to zero when all the hydrogen had been removed. The induction period can be attributed to either (*a*) the autocatalytic nature of the reaction (*vide supra*), or (*b*) the slow removal of the water from the complex. In support of the second view, it was found that the period of induction was reduced and the initial speed of reaction increased by the thorough drying of the copper oxide. With two equal weights of copper oxide, one of which had been exposed to the atmosphere and the other heated at 105° for some time, in the initial stages the latter was reduced at more than twice the speed of the moist sample. The oxide could be made extremely active, and the induction period considerably reduced, if the bulb containing it and the dehydrating agent were evacuated at about 100° and cooled before the addition of dry hydrogen. If, however, the bulb was evacuated and refilled with dry hydrogen when the point of maximum activity had been reached, there was practically no induction period.

Kinetics of the Reaction.—According to the above view the reduction of precipitated copper oxide proceeds in two stages: (*a*) the removal of water, (*b*) the actual reduction. The rate of reduction would be controlled by the slower of these reactions, and by using a large excess of phosphoric oxide and somewhat lower hydrogen pressures, it was hoped to accelerate the first reaction and so obtain a measure of the rate of reduction from the periodic fall of pressure as given by the manometer readings. Many experiments were made, and the following conditions defined. The temperature of reduction in the presence of phosphoric oxide must be below 35° when the hydrogen pressure is 1 atmosphere, otherwise considerable self-heating occurs, and even rapid reduction with glow above 45°. Experiments must be made at low temperatures and hydrogen concentrations, and under these conditions it was observed that after any initial induction period, the rate of change of pressure was proportional to the pressure over a wide range, *i.e.*, $v = -dp/dt = kp_{H_2}$. The reaction rate increased rapidly with rise in temperature, and by making the measurements at 20° and 30° with the same bulb and without disturbing the contents, an average of 2·3 was found for the ratio $k_{30°}/k_{20°}$.

Retardation by Other Gases.—The acceleration of the reduction by the presence of water vapour has been considered. It is known that oxygen has the same effect : Bone and Wheeler (*Phil. Trans.*, 1906, **206**, *A*, 1) found that its influence was nearly ten times as great as that of an equal concentration of nitrogen. In the closed test described in this paper, the addition of such gases as carbon dioxide, sulphur dioxide, acetylene, hydrogen sulphide, or ammonia reduced the rate at which the hydrogen was removed, the magnitude of the effect, however, rapidly decreasing at higher temperatures. These gases possess a residual chemical affinity for copper oxide, and it might be supposed that their protective action is due to the formation of a physicochemical complex as in the case of water. On the other hand, gases such as nitrogen, methane, pentane vapour, or nitrous oxide exerted little more than their dilution effect.

The retarding influence of the former class is made very evident when studied by the phosphoric oxide method at room temperature : the hydrogen in bulbs containing equal weights of copper oxide was diluted with 20% of one of these gases, and the bulbs containing nitrogen, oxygen, sulphur dioxide, and carbon dioxide showed pressure falls of 40·8, 7·7, 6·2, and 6·0 cm. respectively.

These experiments are put forward in support of the above theory that reduction is retarded by the copper oxide water complex. Phosphoric oxide is capable of removing water molecules from the surface of the copper oxide, but is without action on such gases as carbon dioxide, etc., which by their nature can yield new physicochemical complexes. It is also significant that barium oxide facilitates the reduction of copper oxide by carbon monoxide, presumably by removal of the carbon dioxide film.

Autocatalysis.—The above closed tests indicate that there is no incubation period, and any induction period must be of short duration. Experiments were therefore made with copper oxide inoculated with finely divided copper, and the initial rate of reduction was compared with that of pure oxide alone, the conditions of time, temperature, and previous treatment of the oxide being identical. In six experiments at 140° and 10 and 20 minutes' reduction, the maximum difference in reading was only 1 cm. The added copper, however, might be coated with oxide, and so experiments were made in which the oxide was partially reduced in the bulb, and this was evacuated and the oxide plus copper dried in the vacuum. The bulb was then refilled with dry hydrogen, and the pressure–time curves compared with those for pure copper oxide. There was no evidence to show that the copper oxide–copper was reduced with greater velocity even in the initial stages, in such closed tests. These results were confirmed by experiments made at room temperature in the presence of phosphoric oxide, and although it is most difficult to obtain concordant results by this method (*vide supra*), yet sufficient experiments were made against blank tests to prove that copper dust was not an accelerating factor. It is therefore suggested that the main reason for the induction period in the reduction of copper oxide by hydrogen is the removal of the pseudo-combined water from the oxide surface.

Summary.

Precipitated copper oxide was reduced by hydrogen in closed tests and the evidence suggested that there is no incubation and no induction period. When the surface of the oxide was freed from adsorbed gases, the reduction proceeded immediately and with maximum velocity, which is contrary to the view that the action is autocatalytic. The inhibiting action of such gases as water vapour, carbon dioxide, sulphur dioxide, etc., is attributed to the formation of a protective film of a physicochemical nature. If the film is removed by chemical agents, *e.g.*, water by phosphoric oxide, then the reduction of precipitated copper oxide proceeds at room temperature.

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