CLIV.—*Some Experiments on Intensive Drying.*

By RONALD HERBERT PURCELL.

1. *The Influence of Drying on the Reduction of Copper and Bismuth Oxides by Carbon Monoxide.*

MUCH work has been done on the reduction of metallic oxides by carbon monoxide and hydrogen (Jones and Taylor, *J. Physical Chem.*, 1923, **27**, 623), but the effect of removing the last traces of water from the reactants has not previously been demonstrated. In the present paper the effect of drying on the reduction of copper, bismuth, mercury, and silver oxides by carbon monoxide is described; the influence of introducing a small quantity of dry impurity has been investigated in the case of copper oxide; and lastly, the reduction of copper oxide by hydrogen has been examined.

The carbon monoxide was prepared by the interaction of pure redistilled formic and sulphuric acids in an all-glass apparatus, which was a modified form of that used by Tramm (*Z. physikal. Chem.*, 1923, **105**, 356). The gas was washed by two cylinders of alkaline pyrogallol, and then partially dried by pure sulphuric acid. All glass apparatus used was cleaned by filling with nitric–chromic acid mixture which was kept hot for 12 hours. After standing for a further 12 hours, the apparatus was washed out with distilled water, and steam, generated in an all-glass apparatus from distilled water, was passed for 2 hours. Finally, the apparatus was washed with conductivity water and dried in a current of dry air.

The copper oxide was prepared by oxidising pure copper foil in a current of carbon dioxide-free air, the copper being heated to redness in an electric furnace, and precautions being taken to prevent any contamination from the walls of the silica furnace. After being powdered in an agate mortar, the oxide was dried in an apparatus made from Jena combustion glass (Fig. 1), 0·2 g. being placed in each of the side tubes *b*, and the apparatus connected *via* a mercury trap to the vacuum pumps. These, which were used throughout the research, consisted of a Vitreosil mercury-vapour pump and a Hyvac oil-pump. After a preliminary evacuation, some pure phosphoric oxide, sublimed in oxygen at 200° and therefore crystalline and not powdery, was introduced into the side tube *C*, which was at once resealed. The pumps were again started and, apart from the phosphoric oxide compartment, all glass parts were thoroughly baked out. The apparatus was sealed off at the constriction *a*, and the side tubes were placed in an oven where they were continuously heated at 450°, the phosphoric oxide compartment being meanwhile cooled in water. When dry, the bulbs of copper oxide were drawn off at the constrictions (*c*′, *c*″) and sealed into tubes of the form shown in Fig. 2, which could be filled with carbon monoxide. The tubes were cleaned, dried, and connected to the carbon monoxide generator and the pumps. After a preliminary evacuation the apparatus was filled with gas. The end of the tube (*C*) was cut off and, after the introduction of some pure phosphoric oxide, immediately resealed. The tube was baked out under vacuum, filled with carbon monoxide, and again evacuated. The pumps were sealed off at the capillary *a*, and the tube was filled with carbon monoxide to 60 cm. pressure. It was sealed off at *b*, and heated at 400°, the phosphorus pentoxide compartment being meanwhile cooled. In order to examine a tube, the bulb of oxide was broken by allowing it to fall on to the bottom of the tube, the pentoxide compartment

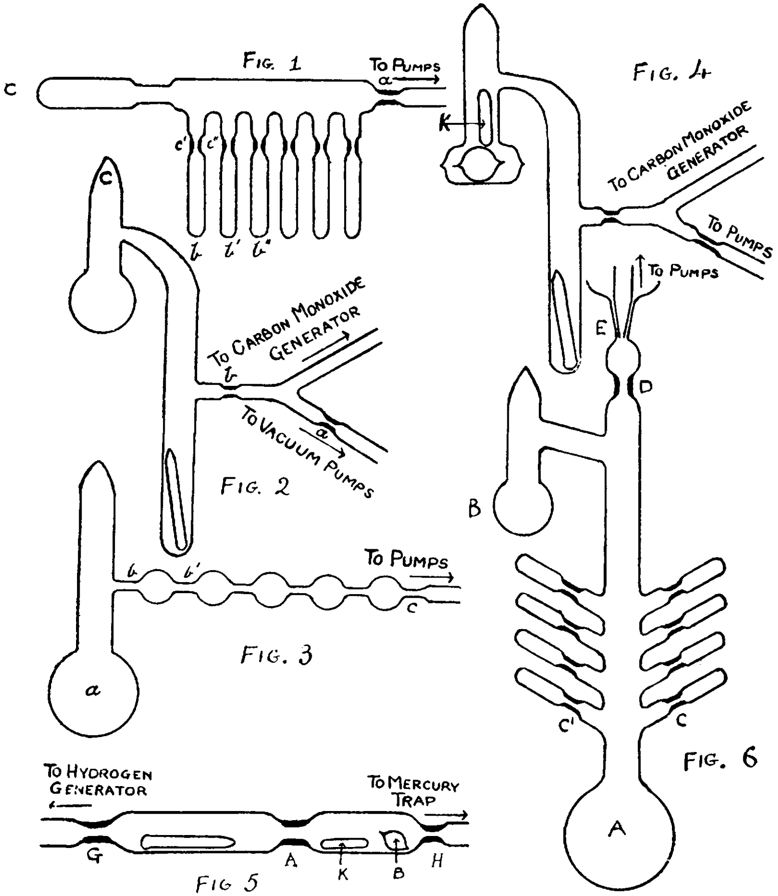
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig 5

Fig. 6

being held below the reaction tube so that none of the drying agent was thrown on the copper oxide. The reduction was followed by the change in colour of the oxide, and since the carbon monoxide was always in excess a mass of red copper was the final product.

Comparison tubes were made in which the phosphoric oxide was omitted. In these the copper oxide was completely reduced by heating at 100° for 90 minutes or at 150° for 10 minutes. When the dry tubes were examined it was found that the temperature required for reaction increased with the time of drying, until a maximum was reached, beyond which further periods of drying had no effect. For instance, after the copper oxide had been dried for 10 days and the carbon monoxide for 7 days, the copper oxide was only reduced after 20 hours at 100° and 90 minutes at 180°. When both the reactants had been dried for a month, reduction would only take place at 425°, and was then complete in 15 minutes. Tubes have been examined in which the carbon monoxide has been dried for 18 months and the copper oxide for 6 months, but the oxide was always reduced at about 425°.

The above experiments were repeated under the same conditions with pure bismuth oxide. In the undried comparison tubes the reduction was complete in $2\frac{1}{2}$ hours at 175° and in a few minutes at 250°. Again it was found that drying decreased the rate of reaction and that the temperature required for reduction increased to a maximum at 430° after 10 weeks' drying.

There are two possible explanations of the above results. Either the oxides react with carbon monoxide at 430° in the absence of water, or appreciable amounts of water are given off by the glass or copper oxide at that temperature. It is possible that the dry carbon monoxide is decomposed into carbon dioxide and carbon on the surface of the oxide, and reduction is effected by the carbon so deposited, since carbon monoxide is known to be decomposed on catalytic surfaces at considerably lower temperatures (Cleminson and Briscoe, J., 1926, 2148). The liberation of water from such a hard glass is improbable at this relatively low temperature, especially in view of the fact that increases in the temperature to which the tubes were heated during drying did not affect the temperature required for reduction.

2. *The Reduction of Mercuric and Silver Oxides by Carbon Monoxide.*

The mercuric oxide was prepared from the metal (purified by prolonged agitation with dilute nitric acid and then thrice distilled) by heating it at 425° in a hard-glass tube with oxygen, which was drawn from a cylinder, passed through a soda-lime tube and a cotton-wool filter, and maintained at 5 atmos. pressure. After a week's heating, the mercuric oxide formed was removed and ground in an agate mortar, any free mercury being removed by heating to 360° in a stream of oxygen.

The oxide was dried in the usual glass apparatus, which was then evacuated, all glass parts being baked out when possible. After sealing off from the pumps, attempts were made to dry the oxide by maintaining it at temperatures between 100° and 300°. When it was thought to be dry, the side tubes were drawn off and sealed into outer tubes which were filled with carbon monoxide. In comparison tubes, from which the phosphoric oxide was omitted, it was found that reduction was rapid at 180°, and this temperature was therefore chosen for examining the dry tubes. Although the oxide was dried for periods of up to 8 months and the gas for one year, in no case was any appreciable difference observed between the dry tube and the damp comparison tube that was heated with it.

Silver oxide was prepared by mixing equimolecular solutions of recrystallised baryta and silver nitrate in conductivity water. The precipitate was rapidly filtered off, washed with conductivity water, and dried over phosphoric oxide in a desiccator. The oxide obtained was reduced by carbon monoxide within 30 minutes at room temperature. Small amounts of it were placed in the usual drying tubes, which were exhausted with cautious heating. Attempts were made to dry the oxide by keeping it for as long as 18 months at 15°, 100°, or 200°, and the bulbs were then sealed into outer tubes in which the carbon monoxide was dried for as much as 6 months. Again, however, it was impossible to detect any change in the rate of reduction on drying.

3. *The Influence of a Dry Third Substance on the Reduction of Copper Oxide by Carbon Monoxide.*

It is of importance to determine how far other substances can act as catalysts in the absence of water, and an attempt has been made to test this in the above reaction, the effect of introducing small amounts of sulphur dioxide, bromine, ether, alcohol, or benzene being observed.

These substances were dried in the apparatus shown in Fig. 3. Some pure phosphoric oxide was placed in bulb *a*, and some of it was sublimed in a stream of dry oxygen into each of the small bulbs. The liquids used were samples of pure materials that had been previously used in intensive-drying experiments. A small quantity was placed in the flask and the neck was sealed off. The apparatus was exhausted while the liquid was cooled in a freezing mixture. After sealing off at *C* from the pumps, the bulbs were sealed off at the capillaries (*b*, *b'*), so that they contained about 2 c.c. of the vapour. With sulphur dioxide, the bulbs were alternately exhausted and filled with gas, and then sealed off so that they contained about 1 c.c. of gas at N.T.P. After drying for about 2 months, the bulbs were sealed into outer tubes as shown in Fig. 4, a bulb of dry copper oxide being placed in the other limb.

The tubes were cleaned and filled with carbon monoxide, the phosphoric oxide being placed in the compartment with the foreign substance. Ten tubes were thus prepared, two for each substance. After drying, the bulbs were broken by the weight *K* and the copper oxide bulb by shaking. The copper oxide in the tubes was then heated at 100° for 24 hours without reduction occurring. There was also no change on heating for 6 hours at 175°, but after 30 minutes at 225°, the oxide in those tubes containing alcohol, ether, and benzene was reduced. The tubes containing sulphur dioxide and bromine were heated without change for 30 minutes at 275°, 325°, and 375°, but at 425° the oxide was reduced in each case. Thus sulphur dioxide and bromine have no power to act in the place of water in this reaction, and the organic vapours appear to catalyse it, though not so efficiently as water. Two possibilities have to be considered; the liquids may begin to undergo incipient decomposition with the copper oxide, or they may have been insufficiently dried, the water introduced with them making the reaction appreciably rapid at 225°.

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

The hydrogen was prepared by electrolysis of a solution of baryta that had been recrystallised ten times and was free from chloride. It was found that the best form of electrolytic vessel was a **U**-tube with platinum electrodes let in from the top, so that the tube could be cooled by water on the outside. The hydrogen was passed over red-hot copper gauze and dried with phosphoric oxide, the gas flow being controlled by a mercury-sealed tap lubricated with phosphoric acid. The copper oxide was dried as previously described, and was sealed into tubes of the form shown in Fig. 5.

This apparatus was connected to the hydrogen generator through a mercury-sealed ground glass joint. A mercury trap and a phosphoric oxide tube prevented air diffusing back. The hydrogen was passed for 4 hours, the glass walls being meanwhile heated. The tube was sealed off while warm at the capillaries *G* and *H*, so that the gas was under slightly reduced pressure on cooling. The bulb of phosphoric oxide, *B*, was broken by the breaker, *K*, and the compartment containing the copper oxide bulb was kept at 400°. When a tube was thought to be dry, it was separated at the constriction *A*, and the bulb of copper oxide broken. It was then heated together with an undried comparison tube. With periods of drying up to 2 years no differences have been observed in the time of reduction of the damp and the dried materials.

5. *A Quantitative Study of the Reduction of Copper Oxide by Carbon Monoxide.*

In the previous experiments the reaction could only be approximately followed by the colour change or by estimation of the carbon dioxide formed after heating for a certain time. Further information was required about the speed of the reaction when it had been materially diminished by drying. This was obtained by passing a stream of dry carbon monoxide over the dry copper oxide and analysing the issuing gas which was collected in 10 c.c. samples. The amount of carbon dioxide in any one sample was regarded as proportional to the mean speed of reaction in the interval while that sample was being collected. An elaboration of the apparatus used by Baker for the combustion of carbon in oxygen was employed for this purpose (*Proc. Roy. Soc.*, 1888, **45**, 1). The carbon monoxide was stored over concentrated sulphuric acid and the gas from this reservoir displaced that from a large flask where it had been dried over phosphoric oxide. This dry gas displaced the intensively dried gas in a second and a third bulb. After passing through a mercury trap to prevent diffusion back into the bulb, it was passed over 1 g. of copper oxide in a boat that could be heated in an electric furnace. A small pump ensured regular flow of the gas, and the mercury valve of this also prevented water vapour diffusing back to the copper oxide. The copper oxide was dried *in situ* by heating to 400° in a vacuum with a phosphoric oxide tube attached.

If the copper oxide were not intensively dried a normal reduction curve was observed. This can be divided into a short period of induction when little or no carbon dioxide is formed, a period when the reduction proceeds at a rapidly increasing rate, and finally a decrease as all the copper oxide becomes reduced. When the reactants were dried, the amount of carbon dioxide formed was much less and it did not become greater with the time. Table I shows the amounts of carbon dioxide found in the issuing gas at the

TABLE I.

Temperature of Oxide, 150°.

Time	90	120	150	195	240	270
CO_2, %	0·5	0·5	0·4	0·6	0·4	0·4

Temperature increased to 196°.

Time	330	350	360	371	410	480
CO_2, %	4·4	4·4	5·0	5·5	5·6	5·5

given time (in minutes from the beginning of the experiment), the reactants having been dried for 7 days. Table II shows the normal curve obtained with the same sample of oxide.

TABLE II.

Temperature of Oxide, 150° (undried).

Time	9	15	30	42	60	87	101
CO_2, %	0·1	0·5	1·4	3·0	9·0	17·0	25·0

Table III gives the constant percentages of carbon dioxide obtained in comparable experiments at different temperatures. The period of drying was in each case one week and the same sample of oxide was used.

TABLE III.

CO_2, %	0·4	0·6	3·0	5·0
Temp. of CuO	150°	160°	180°	195°

Thus it is shown that with the dried reactants the speed of reduction depends on the temperature and the amount of water present. The copper formed does not appear to catalyse the reaction when there is only a very little water vapour present, although it does so when the system has not been dried (Jones and Taylor, *loc. cit.*).

6. *The Effect of Intensive Drying on the Union of Mercury and Oxygen.*

Although mercury can be obtained in a pure state and its physical properties are changed by drying (Baker, J., 1922, **121**, 568), it has not been possible to change its chemical reactivity. Similar negative results have been obtained with some of its compounds; for instance, Baker has found that mercuric oxide decomposes at a normal rate after 20 years' drying, and, as shown earlier, dry mercuric oxide and carbon monoxide reacted normally. Consequently, an attempt was made to observe any change in the rate of formation of the oxide from its elements.

The mercury was purified as previously described and 50 c.c. were placed in the bulb *A* of the apparatus shown in Fig. 6. Some pure phosphoric oxide was introduced into the side tube *B*, which was at once sealed off. The apparatus was baked out under vacuum and then sealed off at the constriction *D*. During the period of drying the mercury in *A* was heated so that it continuously distilled and condensed in the upper part of the tube. Samples of the dry mercury were sealed off in the side tubes *C*, *C'*, and these were sealed into larger tubes similar to those shown in Fig. 5.

The oxygen was prepared by the electrolysis of baryta in an apparatus like that employed for hydrogen. Traces of hydrogen were removed by passage over red-hot copper oxide. The gas was roughly dried by a flask containing concentrated sulphuric acid, and the flow controlled by a mercury-sealed tap lubricated with phosphoric acid.

The tube to be filled was connected to the vacuum pumps and to the oxygen generator *via* a glass diaphragm that could be broken when required. Pure phosphoric oxide was placed in its compartment, which was then sealed off. The tube was baked out in a vacuum, the pumps were sealed off and, after the diaphragm had been broken, filled with oxygen to a little below atmospheric pressure, and the tube was sealed off and heated to 450° to accelerate drying, the phosphoric oxide compartment being meanwhile cooled. After 10 days' heating, the drying of the tube was continued at room temperature. Each tube was examined by drawing off the phosphoric oxide bulb and breaking the tube of mercury; it was then heated together with a damp comparison tube at 400° for 30 minutes and the amounts of oxide formed were compared. Even after 6 months' drying it has not been possible to detect any difference in the rate of formation of the oxide.

Water has been shown to be necessary for a great variety of chemical reactions (H. B. Baker, J., 1894, **65**, 622, *et seq.*), but it is not known what reactions, if any, take place in the absence of water, for failure to observe any change in the velocity of reaction may equally well be ascribed to imperfections in technique. In considering the above results, one is justified in assuming that mercuric oxide is formed from its elements and reacts with carbon monoxide while in a very dry state. It is, however, incorrect to assume that, because a substance is " dry " with respect to one reaction, there is not enough water there for another to proceed normally. This is known not to be the case. For example, carbon monoxide does not explode with oxygen after passing through sulphuric acid, yet a month's drying over phosphoric oxide is necessary to prevent its reducing copper oxide. Also, although Coehn and Tramm have found that samples of hydrogen and oxygen, which did not explode on heating, combined at a normal rate in ultra-violet light, yet Baker and Carlton (J., 1925, **127**, 1990) have shown that the photochemical combination can be influenced by drying. The accumulation of negative results for mercury and its compounds does, however, indicate that they can react in the presence of unusually small amounts of water, a result which is being tested by still further experiments.

The author wishes to express his sincere gratitude to Professor H. B. Baker, under whose direction these experiments were carried out; also to thank the Board of Scientific and Industrial Research for a maintenance grant, and Messrs. Brunner Mond, Ltd., out of whose grant some of the apparatus was bought.

ROYAL COLLEGE OF SCIENCE,
LONDON, S.W. 7.

[*Received, February 28th*, 1928.]