CCLXXXIV.—*The Catalytic Dissociation of Carbon Monoxide.*

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IN 1863, St. C. Deville, experimenting with his "tube chaud et froid," discovered the reversibility of the reaction $CO_2 + C \rightleftharpoons 2CO$ (*Compt. rend.*, 1864, **59**, 873). It was known that heated carbon reduces carbon dioxide to the monoxide, and he observed that when carbon monoxide was heated to about 960° a little carbon dioxide was formed, but above 1000° none could be detected. This is in accordance with general principles, as in the exothermic reaction $2CO \longrightarrow CO_2 + C$ the equilibrium proportion of carbon monoxide would be expected to increase with the temperature. It was early noted (Bell, J., 1869, **22**, 203) that the decomposition is accelerated by the presence of finely-divided metals, such as nickel, cobalt, and iron. This result was further verified by Schenck and his co-workers (*Ber.*, 1903, **36**, 1232, 3663; 1905, **38**, 2139), who found, however, that the oxides of nickel, cobalt, and iron do not increase the velocity of the reaction. Iron, nickel, and cobalt were used as catalytic agents by Boudouard (*Ann. Chim.*, 1901, **24**, 1; *Bull. Soc. chim.*, 1901, **25**, 282, 484) at temperatures of 650°, 800°, and 925°. He found that in presence of these same metals as catalysts the dissociation of carbon monoxide is complete at 445°. Schenck (*loc. cit.*) gave 52·8% as the equilibrium value for this temperature, but it is known that different forms of carbon give widely different values for the equilibrium constant, and this may be the reason for the discrepancy between the results of Boudouard and Schenck.

A table giving the percentage of carbon monoxide in the equilibrium mixture with carbon dioxide in presence of carbon over a range of temperature from 700° to 1200° according to several observers is given by Mellor ("Treatise on Inorganic and Theoretical Chemistry," V, p. 818).

From the foregoing account of the literature, it is apparent that the reaction whereby carbon monoxide yields carbon dioxide and carbon has been fairly thoroughly studied at high temperatures, but it seems to have escaped observation that the same reaction occurs at much lower temperatures.

Preliminary experiments of a qualitative but rigorous nature showed that, whilst pure carbon monoxide in contact with glass and mercury only did not exhibit any shrinkage in volume when kept at 300° for 6 months, the presence of carbon or alumina as catalyst, even at temperatures below 300°, caused carbon monoxide to show a steady contraction in volume which could only be attributed to the reaction $2CO \longrightarrow CO_2 + C$.

The work here described was therefore undertaken to obtain quantitative data as to the rate of the reaction and the final position of equilibrium at relatively low temperatures in presence of a catalyst.

EXPERIMENTAL.

The first series of experiments was directed to ascertaining approximately the minimum temperatures at which carbon, magnesia, and alumina separately as catalysts caused appreciable formation of carbon dioxide in carbon monoxide. The apparatus used enabled carbon monoxide, prepared by dehydration of formic acid and stored over water, to be passed successively through (1) two wash-bottles containing concentrated aqueous potassium hydroxide, (2) two towers containing solid potassium hydroxide, (3) a glass U-tube immersed in an oil-bath which could be maintained at any desired temperature up to 400°, and (4) a wash-bottle fitted with a tap-funnel containing baryta water and provided with a guard-tube, so that clear baryta water could be run into the wash-bottle when it was desired to test for carbon dioxide in the gas issuing from the U-tube. The outlet of (4) communicated with a manometer and a water pump.

In each experiment the whole apparatus beyond the carbon monoxide reservoir was evacuated and then filled with carbon monoxide, and the procedure was repeated four times in succession to ensure the removal of foreign gases. Then, the gas current being maintained at a steady rate, the U-tube was heated to the desired temperature and the baryta water was run into the wash-bottle (4).

The carbon used as a catalyst was sugar-charcoal purified by heating first in chlorine and then in dry hydrogen. Magnesia was prepared by heating magnesium in a stream of oxygen. The alumina was a sample specially prepared for use as a catalyst by Messrs. Peter Spence and Co., Ltd., of Manchester. Before use, the catalysts were heated strongly and cooled in the desiccator.

In a preliminary experiment, the U-tube, containing no catalyst, was maintained at 400° for 4 hours; during the whole of this time the baryta water in (4) remained clear. This affords strong evidence that the reaction $2CO \longrightarrow CO_2 + C$ does not take place at or below 400° when carbon monoxide is in contact with glass surfaces only.

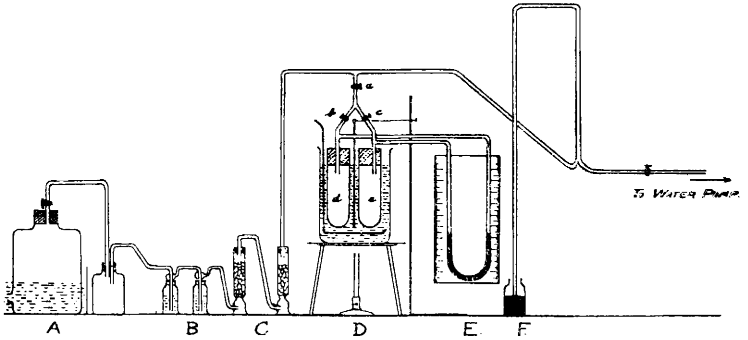
In succeeding experiments with the several catalysts, runs of an hour's duration were made at different temperatures until clear evidence was obtained as to the minimum temperatures at which reaction occurred. These temperatures were: with carbon, 300°;

with magnesium oxide, 290°; and with alumina, 250°. In the last case there were slight signs of the production of carbon dioxide at 215°, but the detection was not definite below 250°.

Making use of the fact that the diminution of volume resulting from the reaction $2CO \longrightarrow CO_2 + C$ is a measure of the extent to which the reaction has occurred, the next series of experiments was designed to ascertain the rate and extent of reaction (1) in the absence of a catalyst, and in the presence of (2) carbon as a catalyst, and (3) alumina as a catalyst.

The apparatus shown in Fig. 1 was attached to the carbon monoxide supply. Taps *a*, *b*, and *c* being open, the whole apparatus was exhausted by means of the water-pump and then filled with carbon monoxide, and by repeating this process of exhausting and filling four times, any residual air was so far removed as to have an inappreciable effect on the observations. The vessels *d* and *e* were surrounded by an oil-bath which was slowly heated and constantly stirred. A blank test confirmed the previous observation that no change in the volume of the gas took place. The U-tube, *e*, was partly filled with mercury, and behind this was placed a millimetre scale so that any rise or fall in the level of the mercury could be measured, and thus any difference of pressure between *d* and *e* observed. During the experiment the taps *b* and *c* were closed, thus isolating the vessels *d* and *e*. The carbon monoxide in the system was initially at a pressure of about 570 mm. Several experiments which need not be detailed agreed in giving definite evidence that with alumina or carbon as a catalyst a definite and considerable diminution of pressure occurred at temperatures below

Fig. 1.

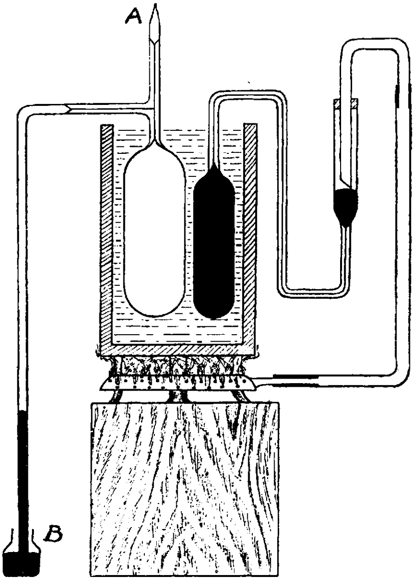


A *Carbon monoxide reservoir.*
B *Aqueous potassium hydroxide.*
C *Solid potassium hydroxide.*
D *Bulbs for carbon monoxide and catalyst.*
E *Mercury gauge.*
F *Manometer.*

300°. The presence of traces of carbon dioxide was proved after each experiment by exhausting the bulbs through a little baryta water.

An attempt was next made to measure the rate of change in pressure that may take place when carbon monoxide is heated with a catalyst, say carbon or alumina, at a constant temperature. For this purpose, as the experiments would necessarily extend over considerable periods, an apparatus entirely of glass in one piece was employed. A bulb of Durosil of about 250 c.c. capacity (Fig. 2) was used and about 2 g. of the catalyst were introduced into the bulb through the capillary tube A. To accomplish this, a tap-funnel was attached to A by means of pressure tubing, and the end B was connected to a water-pump through drying tubes containing potassium hydroxide. By closing the tap of the funnel and starting the pump, a partial vacuum was created in the bulb, then, by closing the end B of the tube and opening the tap of the funnel, the finely-divided catalyst, suspended in pure dry ether contained in the funnel, was washed into the exhausted bulb. The process was repeated until the desired quantity of the catalyst had been introduced. The bulb was placed in a bath of hot water until all the ether had evaporated, and as it was imperative that all traces of vapour should be removed a continuous stream of

Fig. 2.



warm, dry air was afterwards drawn through the bulb for about 8 hours. The apparatus was then connected to the carbon monoxide supply by way of a T-piece attached to A, and was exhausted with the end B dipping under the mercury.

During this process the long arm of the bulb served as a manometer, thus enabling the residual pressure in the bulb to be ascertained. The process of exhausting and filling was repeated four times, the apparatus being filled after each exhaustion with pure carbon monoxide. A simple calculation shows that, the barometric pressure being 736 mm., this procedure should reduce the residual air present after the first evacuation (to 8 mm.) to about 1 part in 7×10^7 parts, whence, making all due allowance for adsorption and other circumstances tending to retain air in the apparatus, it seems safe to conclude that the amount of residual air must be too small to have an appreciable effect on the observations. The first run was carried out at a constant temperature of 250°. A trial run with the bulb before the catalyst was introduced showed that the Durosil glass did not act as a catalyst, no contraction being observed. Such a blank test was carried out with each bulb used subsequently.

In determining the quantity of carbon monoxide present in the bulb for each experiment, the aim was to have the pressure exerted by the gas in the bulb as nearly as possible equal to atmospheric pressure when at the constant temperature at which it was decided to work. This having been achieved, the bulb was sealed off at the top (A) and removed, having its long arm (B) in the mercury reservoir. The bulb was next placed in a bath as shown in Fig. 2.

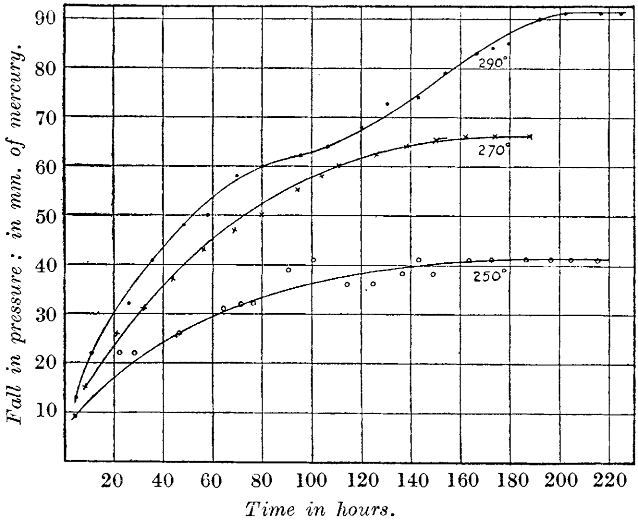
Paraffin " molle " was used in the bath and the constant temperature maintained by a modified form of mercury thermo-regulator indicated in the figure. This design of regulator was adopted because (1) the feed-tube, being outside the bath, was easily adjusted to the required constant temperature, and (2) fluctuations in temperature, due to the evaporation of the mercury, were minimised, as a proportion of the mercury was at a much lower temperature than that of the bath.

A thermometer, reading to 300°, was placed in the bath as shown. The whole of this apparatus was placed in a draught chamber so that the external conditions might be as uniform as possible.

In the first experiment, the bulb, filled with carbon monoxide but containing no catalyst, was heated to a constant temperature of 250° every day for a month; the total duration of heating was 225 hours. During this time, the manometer reading, corrected for variations in atmospheric pressure, showed apparent variations in pressure of the order of 1—3 mm. and always negative. The pressures observed at the last two days of the experiment were within 1 mm. of that recorded at the beginning.

As the whole of the apparatus (bulb, etc.) was in a closed chamber —the surrounding air thus being kept at a rather higher temperature than that of the room—the slight decreases as recorded from time to time appear to be due to contractions in the volume of gas caused by the slight fall in the temperature of the air in the chamber when the readings were taken. This view is supported by the irregularity of the variation. Hence it was concluded that no real decrease in pressure had occurred and that the glass did not act as a catalyst for the reaction at 250°.

FIG. 3.



Carbon was introduced into the bulb, which was afterwards filled with carbon monoxide, all usual precautions being taken (see p. 2151) and a run of 100 hours was made at a constant temperature of 250°. No change of pressure was observed. Another similar run at a constant temperature of 300° gave no evidence of change of pressure in 58 hours. This evidently confirms the previous observation that with carbon as catalyst no carbon dioxide could be detected at temperatures below 300°.

Experiments were next performed with ignited, dry alumina as the catalyst. All due precautions being taken, the bulb was charged with alumina and carbon monoxide. The volume of gas in the bulb was arranged so that the level of the mercury in the manometer was almost equal to the level in the mercury reservoir, the temperature being 250°. The bulb was then kept at a constant temperature of 250° until no further contraction in the volume of the gas took place. After the experiment was ended, the gas in the bulb was exhausted and passed through baryta water. Precipitation took place, proving the presence of carbon dioxide in the bulb.

Similar experiments were carried out at temperatures of 270° and 290°, all necessary precautions being taken in each case.

The results obtained in the three experiments are recorded graphically in Fig. 3.

The present work thus affords evidence that whilst carbon monoxide in contact with clean glass does not appreciably dissociate at 300°, the presence of certain catalysts, notably magnesium oxide and alumina, enables the reaction $2CO \longrightarrow CO_2 + C$ to proceed at temperatures below 300° and, in the case of alumina, as low as 250°. The extent of decomposition of carbon monoxide when equilibrium is attained in presence of alumina increases progressively with rise of temperature in the manner shown by the following figures :

Temperature	250°	270°	290°
Carbon monoxide decomposed (%) ...	5·35	8·50	12·25

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[*Received, May 17th,* 1926.]