CCXLIX.—*The Equilibrium* $CO_2 + C \rightleftharpoons 2CO$.

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FROM an experimental study of reactions taking place in the blast furnace, Schenck and Heller (*Ber.*, 1905, **38**, 2139) concluded that the composition of the mixture of carbon monoxide and dioxide in equilibrium with carbon varied with the modification of carbon employed. Pring and Fairlie (*J.*, 1912, **101**, 91) drew a similar conclusion after studying the equilibrium in the system carbon–hydrogen–methane.

These results, however, do not appear to have received much consideration from workers on the equilibrium between carbon and its oxides, and the contrary opinion, *viz.*, that there is only one position of equilibrium, has been repeatedly expressed, although it is noteworthy that the agreement between the results obtained by the different investigators is by no means good, as the following table shows :

The $CO_2 + C \rightleftharpoons 2CO$ *equilibrium at* $800°$.

Equilibrium composition of gases.		Observer and reference.
CO_2, %.	CO, %.	
7·0	93·0	Boudouard (*Ann. Chim. Phys.*, 1901, **24**, 1).
13·1	86·9	Mayer and Jacoby (*J. Gasbeleucht.*, 1909, **52**, 282).
11·4	88·6	Arndt and Schraube (Diss., Techn. Hochschule, Berlin, 1911).
13·85	86·15	Rhead and Wheeler (*J.*, 1910, **97**, 2178).
9·95	90·05	Bodmer (Diss., Techn. Hochschule, Zurich, 1926).

The results obtained by Clement, Adams, and Haskins (*Bureau of Mines*, Bull. No. 7, 1911) are not given, as they were obtained by extrapolation and were not a direct determination of the system at equilibrium. The method of extrapolation does not appear justifiable, for the results obtained deviate considerably from those given above.

A variation in the carbon modification would be expected to influence the equilibrium, since the different types of carbon are associated with different amounts of energy, and as a result the heat of the reaction $C + CO_2 \rightleftharpoons 2CO$ varies. This heat of reaction for different types of carbon is shown in the following table, together with the corresponding calculated composition of the gases in equilibrium at $800°$.

Type of carbon.	Heat of reaction * (cals. per g.-atom of carbon).	Composition of gases in equilibrium at 800°(calc.).	
		CO_2, %.	CO, %.
Graphite (natural)	41,810	13·8	86·2
Coke	40,490	8·4	91·6
Charcoal	39,480	5·6	94·4
Methane carbon (deposited at 800°)	38,300	3·4	96·6

* These figures have been calculated from the heats of combustion of carbon in oxygen obtained by Roth and Nikitin.

Such calculated compositions are only approximate owing to the lack of accurate specific-heat data over a wide range of temperature, but they serve to show that the variations are of the same order as those between the results of different investigators.

The work described below was carried out because of the absence of any satisfactory experimental measurements showing the influence of the carbon employed on the equilibrium in the system under discussion. All our determinations have been made at 800°; this temperature was chosen as being sufficiently high for the reaction to proceed at a fairly rapid rate, and sufficiently low for the percentage of carbon dioxide at equilibrium to be easily measurable.

FIG. 1.
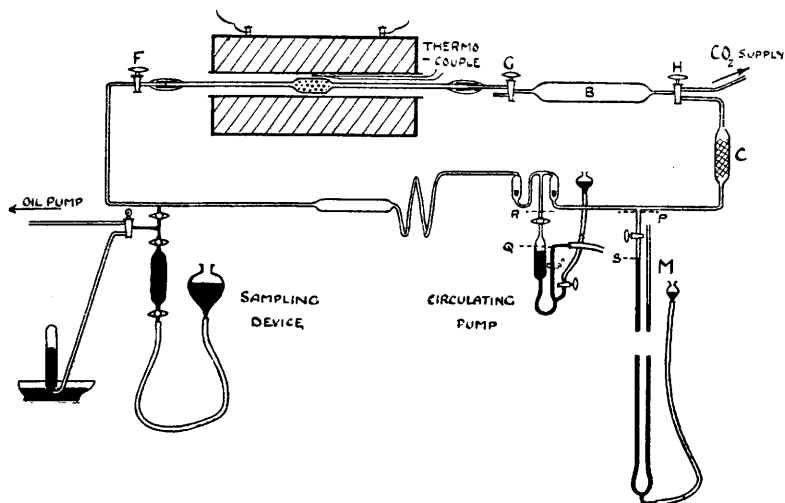
The types of carbon we have used have been : (a) Coke, prepared by carbonising at 800° a fusible Yorkshire coal (Sharlston Wallsend, from the Haigh Moor Seam), containing 35·8% of volatile matter and very little ash (1·2%); (b) graphite, a natural Ceylon product containing 0·4% ash; and (c) charcoal, prepared by carbonising coco-nut shell at 800°. In many experiments the rate of the reaction has been increased by the addition of sodium carbonate (compare Branson and Cobb, Gas Research Fellowship Report, *Trans. Inst. Gas Eng.*, 1927), a procedure which has greatly facilitated this study.

EXPERIMENTAL.

The apparatus used was similar in principle to that employed by Rhead and Wheeler (*loc. cit.*) and is shown in Fig. 1. The method consists essentially in continuously circulating carbon dioxide, and

the carbon monoxide formed by its reduction, over coke kept at
800° in an electric furnace. The whole apparatus is sealed from
the atmosphere, and the progress of the reaction is followed by
observing the rise of pressure in the apparatus. It was assumed
that the reaction had ceased when circulation for a number of hours
produced no further change in the pressure.
A sample of the gas was then taken and
analysed.

FIG. 2a.   FIG. 2b.

Special precautions were taken (a) to cool
the gases rapidly after they had passed over
the carbon, in order to prevent the decom-
position of carbon monoxide; and (b) to
maintain the carbon at a constant temper-
ature throughout the experiment.

Factor (a) is especially important when the
rate of the reaction of the carbon with carbon
dioxide is slow, e.g., when catalysts are not
being employed. In these cases, a furnace
tube of fused silica of the type shown in
Fig. 2a was used. In the constricted ends,
packed, after filling the bulb with carbon,
with rods of silica, the cross-section of the
free space was only 0·05 sq. cm., and conse-
quently the circulating gases passed rapidly
through the zones of decreasing temperature
in the furnace. After an experiment lasting
10 days, there were no signs of any deposition
of carbon arising from the decomposition of
carbon monoxide. When sodium carbonate
was used to accelerate the reaction, a silica
furnace tube could not be employed, but
because of the much greater velocity of the
gasification of carbon the very rapid cooling
of the gases described above was not neces-
sary. In such experiments, a tube of non-
porous Morgan material was used, the free space outside the carbon
column being packed with blocks of the same material. This
arrangement is shown in Fig. 2b. In all experiments, the carbon
was graded $\frac{1}{6}—\frac{1}{10}''$, and for each determination the amount used
occupied a column $2\frac{3}{4}''$ long and $\frac{7}{8}''$ in diameter in the reaction
tube.

The importance of the temperature factor (b) can be seen from
the formula $- Q . dT/T = RT . d \log K$, from which by calculation
it can be shown that a variation of 1° at 800° causes an error of
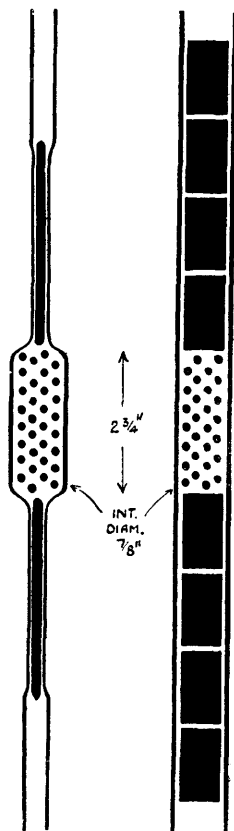
0·1—0·2 unit in the percentage of carbon dioxide at equilibrium. The current control used by Rhead and Wheeler (*loc. cit.*), consisting of two sets of Nernst lamp resistances placed in series in the furnace circuit, satisfactorily damped out the fluctuations in the main's voltage, and enabled the temperature to be maintained constant within $\pm 1°$. The temperature was measured by means of a platinum–platinum-rhodium couple with its junction alongside the carbon column, between the reaction tube and the furnace tube. The remaining details of the apparatus can be seen in Fig. 1.

The furnace tube was connected by thick rubber joints or bungs to the remainder of the apparatus, the rubber being covered with a cement of asbestos and water glass to prevent loss of carbon dioxide by diffusion. It was found that carbon dioxide could be left in the apparatus for 24 hours without any detectable diminution in pressure occurring, and therefore these joints were regarded as satisfactory. All other joints in the apparatus were fused.

The calcium chloride in bulb C (Fig. 1) removed any moisture formed by oxidation of traces of hydrogen given off by the coke or charcoal; between two experiments it was dried by being heated to about 300° in a vacuum. The pressure in the apparatus was observed at manometer M.

Method.—A sample of the carbon under investigation, after being heated for 50 hours in a vacuum at 900° to remove the residual volatile matter, was packed into the reaction tube and the whole apparatus was sealed and evacuated. The furnace temperature was then raised to 800°, and the apparatus was filled with carbon dioxide at a pressure of approximately 40 cm. of mercury. (This was chosen as the initial pressure in order that the final pressure should be approximately 76 cm., but it varied slightly. In the following account, however, all results are calculated to correspond with a pressure of 76 cm. in order to facilitate comparison.) Circulation was then commenced and the pressure was observed every 30 or 60 minutes until it became constant, whereupon a sample of gas was taken.

Experiment 1.—*The influence of heat on the equilibrium over coke impregnated with sodium carbonate.* A sample of coke was heated for 50 hours in a vacuum to drive off residual volatile matter, and then impregnated with sodium carbonate by boiling with a 10% aqueous solution and drying at 105°. By this means, 7·0% by weight of anhydrous sodium carbonate was left on the coke surface.

The equilibrium was determined at 800°, and then the impregnated coke, still in the tube, was heated at 900° under a vacuum for 30 hours. The temperature was lowered to 800°, and another

determination of the equilibrium made. This procedure was repeated until the composition of the gases in equilibrium with the coke at 800° was not influenced by further heating of the coke at 900°. The results obtained are given in Table I.

<div align="center">TABLE I.</div>

Determin-ation.	Total time of heating at 900°.	Time taken to attain equilibrium.	Composition of equilibrium mixture.	
			CO_2, %.	CO, %.
a	50 hours	12 hours	7·0	93·0
b	80 ,,	7 ,,	8·8	91·2
c	110 ,,	15 ,,	10·9	89·1
d	155 ,,	32 ,,	13·5	86·5
e	190 ,,	34 ,,	13·7	86·3
f	250 ,,	55 ,,	13·8	86·2

It is seen that heating a coke prepared from a fusible coal and impregnated with sodium carbonate causes the percentage of carbon dioxide in equilibrium with the coke at 800° to increase from 7·0% to a constant value of 13·8%. The value obtained by Boudouard was 7·0% of carbon dioxide, whilst the constant value of 13·8% coincides within the limits of experimental error with the results obtained by Rhead and Wheeler at the same temperature, and it is noteworthy that the values obtained by other investigators (see p. 1903) lie between these two limits.

The hypothesis is put forward that the gradual alteration in the equilibrium composition of the gases (until the proportion of carbon dioxide reaches 13·8%), which takes place when a coke is heated, is due to a graphitisation of the surface of the coke, and that the variations between the values obtained by different workers are due to the different methods they employed to purify their coke or charcoal before use.

We have shown in other experiments (Gas Research Fellowship Report, *Trans. Inst. Gas Eng.*, 1929) on the influence of heat treatment on the reactivity of coke, that graphitisation takes place most readily on the surface, where the atoms are in the most mobile condition. General graphitisation of the whole coke substance with noticeable increase of the electrical conductivity only takes place with appreciable velocity at temperatures above 2000° (Ruff, *Z. anorg. Chem.*, 1925, **148**, 313; *Z. angew. Chem.*, 1925, **38**, 1164). In these experiments, however, only the surface in contact with the gases determines the position of the equilibrium, and the condition of the interior of the coke has no influence.

Experiment 2.—The equilibrium over graphite in the presence of sodium carbonate. The equilibrium was determined over a sample of natural Ceylon graphite which, in order to accelerate the reaction,

was first impregnated with sodium carbonate.   The values obtained for the equilibrium gas composition in two determinations were :

> (a) 13·85% CO_2; 86·15% CO,
> (b) 13·45% CO_2; 86·55% CO.

The difference between the analyses is small and could have been caused by a variation in the temperature of less than 2°.   It is seen that the gas has the same composition as that in equilibrium over coke which has undergone a prolonged heating.   The results confirm the hypothesis that the effect of heating is to graphitise the surface of the coke.

Experiment 3.—*The equilibrium over charcoal in the absence of sodium carbonate.*   The influence of heat on the equilibrium over coco-nut charcoal was determined without the addition of any foreign substance such as sodium carbonate, this type of charcoal being chosen as a reactive form of carbon.   The results obtained were as follows :

| Charcoal No. | Time of heating. | Heating carried out at | Composition of gas. | |
			CO_2, %.	CO, %.
1	22 hours	850—900°	9·15	90·85
2	50 ,,	900	10·7	89·3
,,	+27·5 ,,	1000	11·0	89·0
,,	+48·0 ,,	1010	12·0	88·0

The results show that the influence of heating the charcoal on the composition of the gas in equilibrium with it at 800° was similar to that observed in Expt. 1 for Sharlston Wallsend coke impregnated with sodium carbonate, in that the percentage of carbon dioxide in the gas was higher the more prolonged and severe the heat treatment.   It is noticed, however, that the percentage of carbon dioxide in the first determination over charcoal (*viz.*, 9·15%) was not so low as in the corresponding determination over the impregnated coke (*viz.*, 7·0%), even although the latter had undergone a more severe heating before these determinations were made.   Comparison of the present data with those of Table I shows also that the surface of coco-nut charcoal did not graphitise so readily on heating as that of the coke, and even after the charcoal had been heated for 75 hours at 1000—1010°, the percentage of carbon dioxide in the gas at equilibrium was considerably less than 13·8—the value obtained in equilibrium over the coke after prolonged heat treatment at 900°.

These results are in agreement with those of other experiments we have made on the reactivity of cokes (*loc. cit.*), which have shown that, other conditions being the same, the more fusible a coal is during carbonisation, the less reactive is the coke produced

and the more easily is the surface of the coke graphitised by heating (see also Ruff, Schmidt, and Olbrich, *Z. anorg. Chem.*, 1925, **148**, 313; Agde and Lynke, " Von den Kohlen und den Mineralölen," 1928).

It is believed that the sodium carbonate, which was present in Expt. 1, but not in Expt. 3, does not cause the surface to graphitise more readily at temperatures below 1000°; indeed, the results of other work indicate that its influence is rather the reverse.   We take the view that, because of an affinity which exists between the sodium carbonate and the free valencies of unsaturated carbon atoms, the presence of sodium carbonate on the surface of the coke tends to prevent such atoms coalescing into an unreactive layer. Thus, there are present on the surface active atoms, which, in the absence of the stabilising effect of the sodium carbonate, would rapidly condense with other carbon atoms into a less active state. As a result of this action, the percentage of carbon dioxide in the gases in equilibrium with coke when sodium carbonate is present, and when the heat treatment has not been too prolonged, is smaller than the percentage of carbon dioxide in the corresponding equilibrium over charcoal in the absence of sodium carbonate (see Expts. 1 and 3).   This difference in the percentage of carbon dioxide at equilibrium is not caused by an inherent difference between charcoal and coke, since, in a determination of the equilibrium over charcoal after 50 hours' heating at 900° in a vacuum and subsequent impregnation with sodium carbonate, the percentage of carbon dioxide at equilibrium was the same as that initially observed over the coke impregnated with sodium carbonate, namely, 7·0%.

Experiment 4.—The equilibrium over coke without the addition of sodium carbonate.   This experiment was carried out in order to ascertain whether the surface of the coke (Sharlston Wallsend) after 50 hours' heating at 900° is graphitic when sodium carbonate is absent.   In this experiment the method was modified because of the slow rate at which the coke reacts with carbon dioxide in absence of sodium carbonate.

Mixtures of carbon dioxide and carbon monoxide containing from 7·0 to 14·2% of dioxide were circulated over the coke for a considerable time.   By trial and error, a mixture was found which did not undergo any change in composition under these conditions. This mixture was taken as corresponding with equilibrium.

Three determinations were made on the same sample of coke in the order given in the following table.   The gas analyses are corrected for any small residue, which was never greater than 0·75%.

Determin-	Composition of initial mixture.		Time of circulation (hours).	Composition after circulation.	
ation.	CO_2, %.	CO, %.		CO_2, %.	CO, %.
a	14·2	85·8	110·0	14·0	86·0
b	9·9	90·1	66·0	12·2	87·8
c	8·3	91·7	162·0	10·5	89·5
Equilibrium gas composition corresponding with graphite 13·8					86·2

The results show that when the percentage of carbon dioxide in the mixture was a little higher than 13·8 (determination a), which corresponds with the equilibrium with graphitic carbon, the carbon dioxide content tended to decrease slightly but was practically constant; when, however, as in determinations b and c, the percentage of carbon dioxide was less than 13·8, circulation caused an increase in the carbon dioxide content.

The results indicate that the surface of the Sharlston Wallsend coke, prepared from a highly fusible caking coal, is graphitic, in the absence of sodium carbonate, after 50 hours' heating at 900° in a vacuum.

Experiment 5.—The influence of gasification on the equilibrium over an impregnated coke. The results of other experiments, carried out at about the same time as the work just described, indicated that the surface of a coke is not homogeneous, some of the carbon being more active than the remainder.

When the coke is heated in a stream of carbon dioxide, the most active portions gasify first, leaving a more unreactive residue, and as a result, the reactivity of a coke generally decreases as gasification proceeds. It is believed that the most active carbon is composed of loosely combined atoms with free valencies and consequently a high energy content. Thus, the average energy content of the surface should diminish as the coke is gasified, and therefore it is to be expected that the compositions of the gas mixtures in equilibrium over the coke before and after partial gasification will be different. The following experiment indicates that this is so.

A sample of coke was impregnated with sodium carbonate after removal of residual volatile matter by 50 hours' heating in a vacuum at 900°, and the equilibrium was then determined over it at 800°. As before, the composition of the gas at equilibrium was CO_2, 7·0% ; CO, 93·0%. The temperature was then raised to 850°, and 1·7 g. of the coke were gasified in carbon dioxide, passing at the rate of 5 litres per hour. The equilibrium was then redetermined at 800°, the composition of the gas being CO_2, 9·2% ; CO, 90·8%. After gasification of a further 0·8 g. of carbon the equilibrium showed no further change. The composition of the gas at equilibrium was CO_2, 9·1% ; CO, 90·9%. These results confirm the view that

gasification first removes preferentially the most active portion of the coke when it is impregnated with sodium carbonate, and after this portion has been consumed, the coke gasifies homogeneously without a further decrease in the average energy content of the carbon.

In order to demonstrate that the difference in the composition of the gas at equilibrium before and after partial gasification was due to the carbon and not to any alteration in the sodium carbonate, the coke residue from the experiment just described was reimpregnated with sodium carbonate and the equilibrium again determined. The composition of the gas at equilibrium was CO_2, 9·15%; CO, 90·85%.

Conclusions.

The results of the experiments described indicate that the nature of the carbon influences the equilibrium in the system carbon–carbon dioxide–carbon monoxide.

Values for the percentage of carbon dioxide in the gas at equilibrium at 800° and 1 atm. pressure vary from 7·0 to 13·8%, according to the carbon used and its pre-treatment.

It appears that 13·8% of carbon dioxide corresponds with saturated graphitic carbon, and that the lower figures are obtained when carbon containing active unsaturated atoms is present.

The effect of gasifying an impregnated coke, which consists of a mixture of carbons having varying degrees of unsaturation, is to remove preferentially the most active unsaturated constituents, leaving a less active residue.

Heating a carbon containing unsaturated atoms with a high energy content gradually transforms these into more stable atoms corresponding with a higher percentage of carbon dioxide at equilibrium. Some types of carbon undergo this change more readily than others, and it is minimised by impregnation with sodium carbonate.

Owing to this effect of heating on a carbon, in a determination of the equilibrium over a carbon such as charcoal at a high temperature, if the gases were circulated for a sufficiently long time, the final equilibrium would be the same as that obtained over graphite. The final equilibrium so obtained cannot, however, be regarded as proper to the original carbon, and it is to be remembered that graphitisation is a slow process compared with the gasification of carbon in industrial or domestic use.

We have taken the view that the presence of sodium carbonate is without effect on the equilibrium between carbon dioxide and monoxide over carbon, except in so far as it influences the nature

of the carbon surface exposed to the gases, and that at a given temperature and pressure the equilibrium depends solely on the energy content of the carbon atoms on the surface. This opinion is supported by the results of Expts. 1, 2, and 5, which show that the composition of the gases at equilibrium varies with the type of carbon used and its pre-treatment, even when the amount of sodium carbonate present is the same, and also by the agreement of the results we have obtained, using (a) impregnated coke after a prolonged heating and (b) impregnated graphite, with those obtained at the same temperature by Rhead and Wheeler, üsing purified wood charcoal which had undergone considerable heat treatment.

The structure of the solid carbon formed by various decompositions and transformations has been the subject of several recent investigations, and the results are relevant to the present issue. Unfortunately, they differ among themselves. For example, Hofmann (*Ber.*, 1926, **59**, *B*, 2433) concludes that charcoal is a crystalline carbon in which the crystals are very small, whilst Ruff and his co-workers (*e.g.*, *Z. anorg. Chem.*, 1925, **148**, 313) conclude that amorphous carbon as an individual modification is in better agreement with the influence of heat upon it, and that when charcoal is heated, its properties do not change continuously to those of graphite, but in stages.

It should be noticed that, whereas Hofmann investigated carbons formed by deposition from the gaseous phase, Ruff's work was carried out on carbon prepared by the decomposition of a solid, which, during the decomposition, did not liquefy or vaporise. Thus, while it is conceivable that atoms in deposited carbons are regularly arranged in the graphitic lattice, it is equally conceivable that in charcoal prepared from a substance in which originally the carbon atoms are certainly not so arranged, a stage is passed through in which the substance can be rightly classed as " amorphous."

As the work of Hofmann (*loc. cit.*) showed that carbon deposited from carbon monoxide is crystalline, the size of the crystals and consequently the heat of combustion of the carbon varying with the conditions of decomposition, it is to be expected that the composition of the mixture of carbon dioxide and monoxide at equilibrium in the system $C + CO_2 \rightleftharpoons 2CO$, when determined by the decomposition of carbon monoxide, will vary with the nature of the deposited carbon, as it does when the equilibrium is approached from carbon and carbon dioxide.

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