CCXXVI.—*The Effect of Temperature on the Equilibrium* $2CO \rightleftharpoons CO_2 + C$.

By Thomas Fred Eric Rhead and Richard Vernon Wheeler.

The fact that carbon monoxide dissociates under the influence of heat, yielding carbon dioxide and carbon, or, in other words, the fact that the reaction:

$$CO_2 + C = 2CO$$

is reversible, was discovered by H. Sainte-Claire Deville in 1864 (*Compt. rend.*, 1864, **59**, 873; 1865, **60**, 317) by means of his "hot-cold" tube. He was able to observe only a small degree of dissociation at a temperature a little lower than the melting point of silver, whilst at temperatures above 1000° none at all could be detected.

Since it was assumed that the degree of dissociation of carbon monoxide, like that of carbon dioxide and steam, should increase with increased temperature, doubt was cast on Deville's first experiments, and it was suggested that the formation of carbon dioxide and the deposition of carbon were due to the chemical action of the glaze of the porcelain tubes he employed.

In 1869 Sir Lothian Bell (*Journ. Chem. Soc.*, **22**, 203), while studying the reactions taking place in the blast-furnace, found that such portions of the iron ore as had been subjected to the action of carbon monoxide at comparatively low temperatures in the upper part of the furnace were impregnated with carbon, presumably arising from the dissociation of the gas. He thereupon instituted laboratory experiments to determine the action of carbon monoxide on different oxides at different temperatures.

As a result of these experiments, Bell was able to state that the reduced metal was as effective as the oxide in determining the decomposition of carbon monoxide, and he gave the equation of the reaction as being:

$$2CO = CO_2 + C.$$

He also showed that the oxides of nickel and cobalt and the reduced metals acted in a similar manner to iron oxide and reduced iron.

The influence of temperature on the amount of decomposition in a given time was also studied by Bell, comparative figures being obtained from the quantities of carbon deposited. This is well shown in the following series of experiments, in which carbon

monoxide was passed slowly over reduced iron at different temperatures during six hours:

Temperature		250°	400°	500°	600°	800°
Carbon deposited.	Grams per 100 grams of iron	4·7	181	95	6	0·3

It is thus apparent that a low temperature favours the decomposition, a result which explains the failure of Deville and others to obtain evidence of dissociation at 1000°, and is in accordance with the fact that the reaction $2CO = CO_2 + C$ is exothermic. The heat of reaction is shown by the following equations:

(1). $CO + O = CO_2 + 68{\cdot}0$ Kg.C. units.
(2). $C + O = CO + 29{\cdot}0$,, ,,

whence $2CO = CO_2 + C + 39{\cdot}0$,, ,,

Since the reaction is reversible, an equilibrium must be established between the quantities of carbon dioxide and monoxide that can exist together in the presence of carbon; and, in accordance with van't Hoff's principle of mobile equilibrium, the quantity of carbon monoxide will be increased by lowering the temperature.

The equilibrium at different temperatures has been studied by O. Boudouard (*Ann. Chim. Phys.*, 1901, [vii], **24**, 5), who has given figures for 650°, 800°, and 925°.

In studying the reaction $2CO \rightarrow CO_2 + C$, Boudouard made use of iron, nickel, and cobalt as catalysts. The finely divided metals were obtained by impregnating broken pumice with the nitrates and igniting, the oxides thus formed being afterwards heated in a stream of carbon monoxide until reduction was considered to be complete.

For the experiments at temperatures below 700°, glass tubes, 6 to 7 cm. long and 1·5 cm. in diameter, were used, the total volume of gas being from 12 to 15 c.c. Above 700°, a porcelain tube, 40 cm. long and of 2·4 cm. internal diameter, was employed, the pumice containing the catalyst occupying the middle 10 cm. of the tube, and the remainder being packed with broken porcelain.

The main results were as follow:

Temperature.	Catalyst.	Duration of heating.	Carbon dioxide, per cent.
445°	iron	6 hours	100
445	nickel	1 hour	100
445	cobalt	1 ,,	100
650	cobalt	7 ,,	61
800	nickel	4 ,,	6·7
800	cobalt	4 ,,	6·5

In one experiment at 445°, using a very small quantity of iron oxide (reduced by carbon monoxide) as catalyst, Boudouard obtained 52·3 per cent. of carbon dioxide and 47·7 per cent. of carbon monoxide remaining after six hours' heating.

The reverse reaction, $CO_2 + C \rightarrow 2CO$, was studied in a similar manner, but without the use of catalysts, purified wood charcoal being employed. The carbon was heated in an atmosphere of carbon dioxide in tubes sealed at one end, with the other end open and bent so as to dip under mercury, the object being to avoid bursting of the tubes due to increased pressure as the reaction proceeded.

The results were as follow:

Temperature.	Duration of heating, hours.	Carbon dioxide, per cent.
650°	9	62·4
650	12	61·5
800	6	6·7
800	6	6·3

In addition to the above, two experiments were made at 925°, in which a measured volume of carbon dioxide was passed in a slow stream through the heated charcoal, and the resulting gases bubbled through baryta water, the barium carbonate that was precipitated being afterwards weighed. Assuming that a single passage of the carbon dioxide over the heated charcoal was sufficient to establish equilibrium, Boudouard calculated from one experiment 3·3 per cent., and from the other 4·5 per cent., of carbon dioxide remaining in equilibrium with carbon monoxide over carbon at 925°.

Boudouard's experiments prove that the equilibrium ratio CO/CO_2 in contact with carbon is a function of temperature, and the results are in general agreement with the laws respecting equilibria in gaseous systems.

R. Schenck and F. Zimmermann (*Ber.*, 1903, **36**, 1), while studying more particularly the order of the reactions taking place, have been able to prove that the oxides of iron, nickel, and cobalt are quite ineffective in determining the dissociation of carbon monoxide, and that it is only the reduced metals that act catalytically. This is in direct opposition to the views advanced by Boudouard. At the same time Schenck and Zimmermann give results for the equilibrium at low temperatures (445° and 508°) that are entirely at variance with those of Boudouard. At 445° Boudouard regards the dissociation of carbon monoxide as complete; while Schenck and Zimmermann, using reduced iron as catalyst, obtained 52·8 per cent. of carbon monoxide as the quantity remaining in equilibrium at that temperature. It is interesting to note that this figure agrees fairly well with that obtained by Boudouard when using only a small quantity of iron as catalyst (a result which he discards), and it seems probable that in those experiments, otherwise inexplicable, in which he obtained complete decomposition of carbon monoxide, the oxides of the metals used as catalysts were incom-

pletely reduced before the tubes were sealed, and that oxidation of the carbon monoxide took place.

We considered it desirable to determine the equilibrium ratio more accurately and for a greater number of temperatures, avoiding the use of catalysts, for Boudouard's method of experiment did not appear to us to be calculated to give very accurate results, and his figures were not in agreement with those obtained by us during the course of an investigation on the mode of burning of carbon on which we are still engaged.

The method we have adopted has been to circulate carbon dioxide continuously over purified wood charcoal packed in a porcelain tube, and heated in an electric resistance furnace.

We have obtained in this manner the following figures for the percentages of carbon dioxide and monoxide that are in equilibrium in the presence of excess of carbon at different temperatures:

Temperature.	Carbon dioxide. (Per cent. by volume.)	Carbon monoxide. (Per cent. by volume.)
850°	6·23	93·77
900	2·22	97·78
950	1·32	98·68
1000	0·59	99·41
1050	0·37	99·63
1100	0·15	99·85
1200	0·06	99·94

The percentages are calculated as those of the nitrogen-free gases. The gases usually contained from 1 to 2 per cent. of nitrogen.

In Le Chatelier's general formula for equilibrium in gaseous systems:

$$500\int L\frac{dT}{T} + (N' - N)\log_e P + \log_e \frac{c_1^{n_1} c'_1{}^{n'_1}\ldots}{c_2^{n_2} c'_2{}^{n'_2}\ldots} = k$$

L = the total heat of the reaction at absolute temperature T.

P = the pressure in atmospheres.

N and N' = the number of molecules on the left- and on the right-hand side of the equation.

n_1, n'_1,... and n_2, n'_2,... = the number of molecules of the different substances taking part in the reaction, index 1 meaning the initial and index 2 the final system.

c_1, c'_1,... and c_2, c'_2,... = the concentrations of the different substances, indices as above.

In the system:

$$2CO \rightleftarrows CO_2 + C$$

$n_1 = 2$; $n_2 = 1$; $n'_2 = 0$; $c'_2 = 0$.

If the system is in equilibrium at atmospheric pressure, $P = 1$, and the expression

$$(N - N')\log_e P = 0.$$

Assuming with Le Chatelier that the heat of reaction is constant, and introducing its value (39·0 Kg.C. units), the equation then becomes:

$$\frac{19{,}500}{T} + \log_e \frac{c_1^2}{c_2} = k.$$

The values for k calculated from our results are as follow:

T.	c_1.	c_2.	k.
1123°	0·9377	0·0623	20·01
1173	0·9778	0·0222	20·39
1223	0·9868	0·0132	20·24
1273	0·9941	0·0059	20·44
1323	0·9963	0·0037	20·32
1373	0·9985	0·0015	20·70
1473	0·9994	0·0006	20·65

Experimental.

The Equilibrium Furnace.—In designing the equilibrium furnace, the two chief considerations were (*a*) the obtaining of a uniform temperature, and (*b*) the attainment of rapid cooling of the gases after they had left the zone of reaction, in order to "fix" the equilibrium. We had, moreover, to recognise the fact that at temperatures above 1000° both porcelain and fused silica or quartz tubes, such as we intended to employ for the reaction vessel, become slightly porous to gases.

The construction of the furnace, which was made for us by Messrs. C. W. Cook and Co., at the University Engineering Works, Manchester, is shown in Fig. 1. It consists essentially of a glazed Berlin porcelain tube, 51 cm. long and of 28 mm. external and 20 mm. internal diameter, wound with platinum wire, through which an electric current can be passed. The winding is arranged so as to give a uniform temperature throughout the central portion of 12 cm., and is carried on either side close up to the gunmetal water-jackets, *J*, being insulated from them by thin disks of porcelain. By winding the coils closer near each end than along the rest of the tube, we are able, when a fairly rapid stream of water is passing through the jackets, to obtain a sudden reduction in the temperature of the tube from 1000° in the central uniform portion to 400° or less within a distance of 1·5 cm., while the temperature falls to below 150° within a distance of 5 cm.

This result is not attained solely as the effect of water-cooling and increasing the length of resistance wire at the ends, but is in part due to the double-jacketing arrangement, *A*, which is intended primarily to avoid any error due to porosity of the porcelain tube at high temperatures. A nickel tube, 22 cm. long and of 7·1 cm. external and 5·7 cm. internal diameter, is fixed coaxially with the

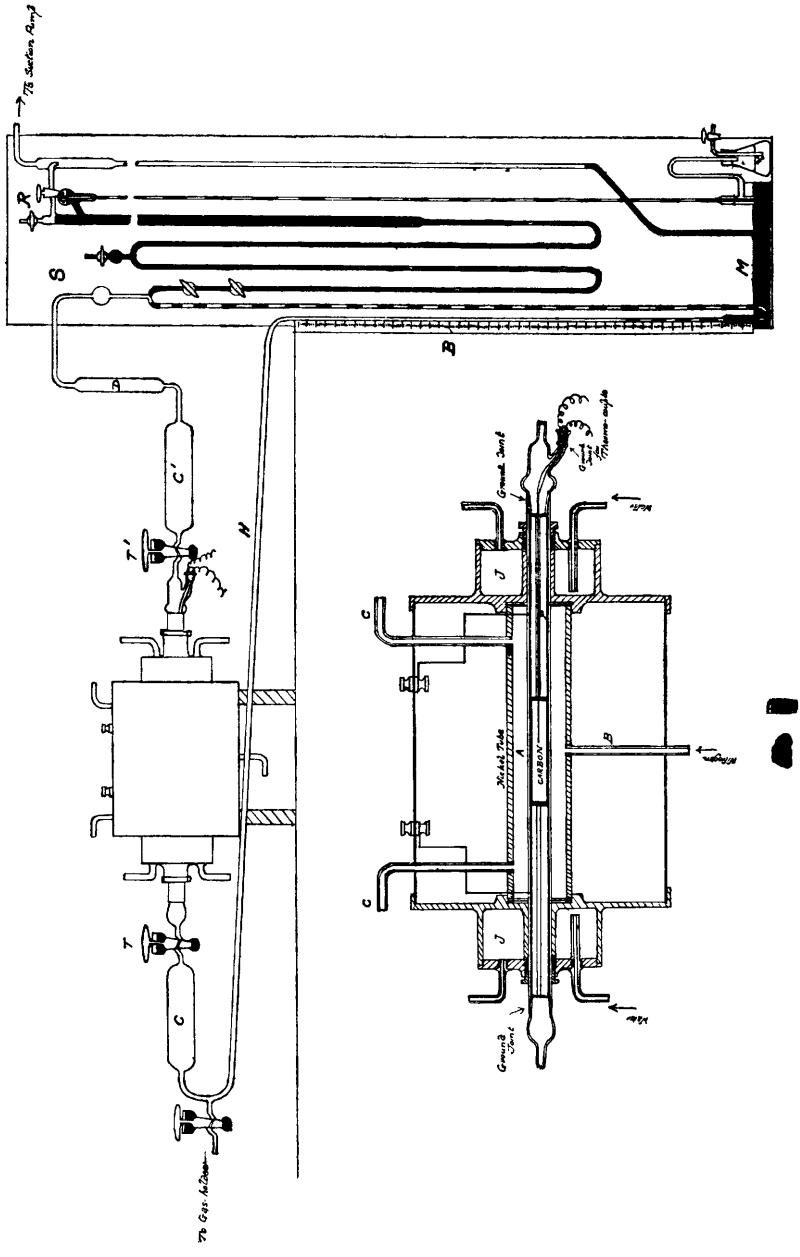


FIG. 1.

porcelain tube, and through the annular space a slow stream of dry nitrogen is passed. The nitrogen, prepared by Harcourt's method, enters under a slight pressure through the central tube *B*, and issues at *C*, *C* through wash-bottles containing concentrated sulphuric acid. The passing of this stream of dry nitrogen, in addition to ensuring that no oxygen or water vapour enters the porcelain tube if it becomes porous at high temperatures, causes a more uniform distribution of heat throughout the length of the furnace, an effect which is enhanced by the position of entrance of the gas.

The furnace tubes are surrounded by a thick layer of kieselguhr to prevent loss of heat by radiation, and the whole is encased in a jacket of sheet iron.

The carbon used throughout this research has been wood charcoal purified by first digesting with concentrated hydrochloric acid (in a bolt-head flask fitted with a reflex condenser) to remove the ash; washing with distilled water; and subsequently heating at 1000° in a stream of dry chlorine, washing, heating in a stream of hydrogen, and finally in a vacuum at 1000° for forty-eight hours. It is crushed and sieved so as to pass through a 10-mesh sieve and remain on a 20-mesh, and about 6 grams are then loosely packed into a thin tube of quartz, 12 cm. long and open at both ends, which slides easily into the porcelain tube.

After the insertion of the quartz sheath containing the carbon, a plug of silica, 16·5 cm. long and 1·9 cm. in diameter with a hole 3 mm. in diameter drilled through the centre, is introduced at each end. These plugs serve to keep the carbon surface in position in the zone of constant temperature, but they are intended more especially to cause the stream of gases, after passing over the heated carbon, to pass rapidly out of the tube, and thus ensure that the equilibrium determined shall be that of the experimental temperature recorded.

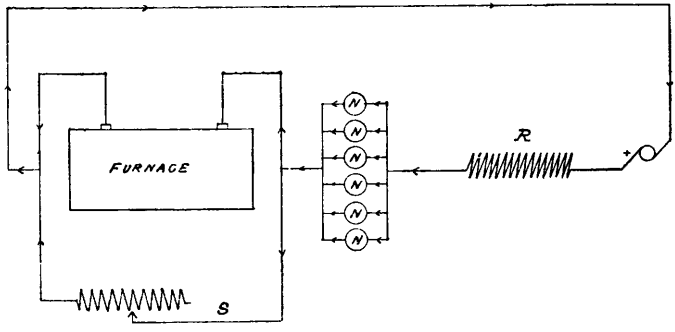
The Measurement of Temperature.—The temperatures are measured by means of a platinum and platinum-rhodium thermocouple, and recorded by one of the Cambridge Scientific Instrument Company's "Thread-Recorders." The couple is embedded in the middle of the carbon, the leads being insulated by thin quill tubing of quartz, and the whole enclosed in a sheath of thin quartz, which passes easily through the bore of the plug *P*.

Some little difficulty was at first experienced in maintaining a constant temperature, owing to fluctuations in the voltage of the electric current supplied to the furnace. Since the experiments extended continuously over several days, or, in some cases, several weeks, personal attention was found to be impossible, and a means

had to be devised of automatically regulating the voltage. The method finally employed, for the suggestion of which we are indebted to Mr. E. Muller, of the Cambridge Scientific Instrument Company, is as follows.

The voltage of the main current is first cut down by the large resistance, R (Fig. 2), to within a small margin of that required to obtain the experimental temperature in the furnace. It then passes through the Nernst lamp steadying resistances, N, of which a sufficient number are arranged in parallel to allow the requisite quantity of current to pass round the circuit. These steadying resistances take as their normal current 1 ampere at 15 volts, whilst the furnace, when hot, takes about 3 amperes. The exact number that are required to ensure perfect regulation and automatic adjustment of the voltage across the furnace terminals depends on the experimental temperature employed; there must be a sufficient

FIG. 2.



number to ensure that the spirals of fine iron wire within the exhausted globes of each shall glow a dull red without becoming overheated; for they depend for their action on the change in electrical resistance that occurs in iron wire at a temperature of about 775°.

After passing through the Nernst lamp resistances, the current is divided, part going through the furnace, and part through the shunt, S, containing a rheostat. About equal quantities of current pass through the furnace and the shunt. The final adjustment of the voltage across the furnace to that required to obtain a given temperature is made by means of the rheostat in the shunt, the alteration of which does not interfere with the main current, since the whole of it passes through the Nernst lamp resistances.

This method has proved eminently satisfactory, the experimental temperature being maintained without any serious fluctuations continuously during several weeks.

General Arrangement of Apparatus.—The reacting gases are circulated without interruption over the heated carbon until equilibrium is attained. The general form of the circulation apparatus is that designed by one of us in conjunction with W. A. Bone for the investigation of the slow combustion of hydrocarbons (Trans., 1903, **83**, 1074).

The porcelain tube containing the carbon carries a ground glass joint at each end held firmly in position by strong springs. These joints make connexion on either side, through the mercury-cup taps T, T' (Fig. 1), with the cylindrical vessels C, C', each of 200 c.c. capacity. These vessels mainly determine the capacity of the apparatus, and are cylindrical in form in order to allow of being heated to drive off any traces of gas that may have a tendency to stick to the glass.

On the right-hand side, connexion is made, through the calcium chloride drying-tube D, to the head of the Sprengel pump S. On the left is fused a long tube of wide bore, which passes horizontally across the front of the furnace and is then bent downwards at right angles, forming a manometric tube, which stands over the delivery-tube of the Sprengel pump in the mercury trough M. A short T-piece near the left-hand cylinder, closed by a mercury-cup tap, serves for the introduction of the gas.

With the exception of the ground joint connexions to the porcelain tube, the apparatus is of fused glass throughout.

The gases are drawn, by means of the automatic Sprengel pump, through the furnace, and delivered under mercury in the trough M into the manometric tube B, whence they return along the horizontal tube H to the cylinder C, and are again drawn forward through the furnace. The automatic Sprengel pump, the general construction of which is described in the paper referred to above (*loc. cit.*, p. 1079), is actuated by suction produced by a double-acting Geryk pump driven by an electric motor, and is so arranged that the head of mercury in the reservoir R allows of the gases being circulated at atmospheric pressure.

The total volume of the apparatus, measured at 0°, is 570 c.c.; that of the packed porcelain tube 96 c.c.

The Gas Analyses.—The carbon dioxide was prepared by dropping boiled concentrated sulphuric acid from a separating funnel into a boiled solution of sodium carbonate contained in an Erlenmeyer flask. The gas evolved was passed through two sulphuric acid worms, and collected in a glass gas-holder containing concentrated sulphuric acid, over which it was stored for two weeks before being used for an experiment.

The carbon monoxide was prepared from sodium formate, made

into a stiff paste with distilled water, by the action of concentrated sulphuric acid. It was washed through two worms containing potassium hydroxide solution, and stored over sulphuric acid in the same manner as the carbon dioxide.

The gases remaining after an experiment were analysed volumetrically in a Bone and Wheeler gas analysis apparatus over mercury, from 200 to 300 measures of gas being taken for an analysis. Carbon dioxide was estimated by absorption with as small a quantity of aqueous potassium hydroxide as possible, or when only small quantities were present, by absorption with a concentrated solution of barium hydroxide. Carbon monoxide was absorbed by an ammoniacal solution of cuprous chloride, prepared by passing ammonia gas into distilled water containing the freshly precipitated cuprous chloride in suspension until the latter was dissolved. A little ammonium chloride was added to the solution as thus prepared to reduce the tension of ammonia vapour. The gas was treated twice with small quantities of this solution, and afterwards washed with dilute sulphuric acid.

Any residue (which never amounted to more than 2 per cent. of the total gas) was afterwards exploded with a measured volume of air and oxygen, to which a few c.c. of pure electrolytic gas were added. Any contraction in volume after explosion, or after absorption with potassium hydroxide, was then determined. A trace of hydrogen due to insufficient drying of the gases, or to moisture in the circulation apparatus, was detected in several experiments the results of which were discarded.

Method of Conducting an Experiment.—The apparatus having been thoroughly exhausted, the glass being heated in a large blow-pipe flame to drive off the last traces of air, the carbon dioxide (or monoxide) is introduced in such quantity that when the reaction is complete the gases shall be as nearly as possible at atmospheric pressure. As a preliminary to a series of experiments, a certain quantity of carbon dioxide is introduced to the carbon heated to 1000° and allowed to circulate for several days. The resulting gases are then pumped out, and the furnace brought to the experimental temperature. This preliminary treatment serves to remove any traces of water-vapour that still remain in the apparatus; it was in the gases resulting from such experiments that we were able to detect traces of hydrogen.

In the experiments proper the gases are allowed to circulate for twenty-four hours after the volume, as indicated by a scale fixed behind the manometric tube, has ceased to change. The reaction tube is then shut off from the rest of the apparatus, and samples are withdrawn for analysis.

Results of Experiments.

The results of our experiments can best be expressed in tabular form as follow:

Experiment number.	Temperature.	Duration of heating, hours.	Composition of resulting gases (calculated as nitrogen-free mixture). CO_2.	CO.
E 14	850°	240	6·23	93·77
E 9	900	180	2·22	97·78
E 16	950	144	1·32	98·68
E 4	1000	48	0·59	99·41
E 18	1050	48	0·37	99·63
E 5	1100	48	0·15	99·85
E 6	1200	48	0·06	99·94

In addition, we have made two attempts to attain equilibrium at a temperature of 800° with the circulation apparatus, but have abandoned the experiments after they had continued for six weeks without showing signs of coming to a conclusion, 20 per cent. of carbon dioxide still remaining after that time.

Boudouard, in the reduction of carbon dioxide by wood charcoal without the presence of a catalyst, states that equilibrium was attained in his experiments after six hours' heating at 800° and after twelve hours' heating at 650°, the percentages of carbon dioxide remaining in equilibrium being 6·3 and 61·5 per cent. respectively at the two temperatures. The volume of his apparatus was only from 12 to 15 c.c. as against our 570 c.c., but we do not think that this fact is sufficient to explain the marked discrepancy between our results, since we used a correspondingly larger quantity of carbon surface. In another series of experiments that we are making on the rate of reduction of carbon dioxide by wood charcoal at different temperatures, we have been unable to obtain a disappearance of carbon dioxide of more than 0·7 per cent. after 122 hours' heating at 700°.

All our experiments recorded above have been made starting with an initial concentration of 100 per cent. carbon dioxide; for the rate at which the reverse reaction proceeds was too slow to enable us to attain equilibrium in a reasonable time without the presence of a catalyst, the use of which we wished to avoid.

The relative rates of the two reactions during the initial stages are well shown in the experiments recorded below. A temperature of 850° was chosen as being that at which the reduction of carbon dioxide by carbon was fairly rapid, and the dissociation of carbon monoxide readily appreciable.

The rates of the reactions are calculated, by means of the relation

$$\frac{1}{t} \log \frac{C_o}{C_t} = k,$$

from the partial pressures (concentrations) of the carbon dioxide at different time intervals in experiment R 13, and from the partial pressures of the carbon monoxide in experiment R 15:

Experiment R 13.

$CO_2 + C = 2CO$. Temperature 850°.

Time. (Unit = 1 hour).	P. at 0°.	P_{CO_2}.	k_{CO_2}.
0	258·6	257·6	—
1	292·3	224·9	0·0590
2	317·8	199·4	0·0555
4	356·3	160·9	0·0511
6	389·0	128·2	0·0505
8	415·8	101·4	0·0506
12	439·5	77·7	0·0434

Experiment R 15.

$2CO = CO_2 + C$. Temperature 850°.

Time. (Unit = 1 hour).	P. at 0°.	P_{CO}.	k_{CO}.
0	463·0	453·7	—
24	459·2	446·1	0·00030
48	453·9	435·5	0·00037
72	452·1	431·9	0·00030
96	448·0	423·7	0·00031
120	447·2	422·1	0·00026

It will thus be seen that the reduction of carbon dioxide by carbon takes place at 850° at a speed 166 times as great as the dissociation of carbon monoxide at the same temperature.

We may incidentally draw attention to the fact that the good agreement of the constant k, calculated from the expression $\frac{1}{t}\log\frac{C_o}{C_t}$ for a unimolecular reaction, points to both reactions being essentially surface phenomena; the rate of reduction of carbon dioxide and the rate of dissociation of carbon monoxide both varying directly with the partial pressure of the gas. It is our intention to discuss this question more fully when we have concluded a research, on which we are at present engaged, on the relative rates of reaction between carbon dioxide, carbon monoxide, oxygen, and carbon at different temperatures.

This work has been undertaken in connexion with the experiments now being carried out by the Mining Association of Great Britain on coal-dust explosions. We are extending it to the investigation of the influence of pressure on the equilibrium ratio.

ALTOFTS.