[Contribution from Coal Research Laboratory, Carnegie Institute of Technology]

The Rate of Reduction of Carbon Dioxide by Graphite

By Martin A. Mayers

In spite of its technical importance, the rate of reduction of carbon dioxide by carbon has not been accurately determined. Although this reaction has been used to measure the reactivity of cokes and other forms of carbon,[1] the data of these measurements cannot be recalculated to determine specific rates of reaction. For this purpose, reactivity measurements are deficient in that the methods used permit large unknown changes in the concentrations of the reacting gases during their passage over the reacting surface; no criteria are provided for the elimination of concentration gradients and the concomitant diffusion effects; and, in most cases, the carbon is used as a bed of granules, so that no accurate estimate can be made of the surface exposed.

The reaction may be controlled easily because of its endothermic nature and is, therefore, well suited to experimental determination of its rate. It is of additional interest in that it may provide information concerning the action of the surface carbon–oxygen complex found by previous workers to be of importance in the combustion of carbon by air or oxygen.

Experimental Conditions

In order to determine the specific rate of reduction of carbon dioxide the following four conditions must be satisfied: (1) the sample must have a known gross surface exposed to the action of the gas, (2) the gas pressure must be known, constant over the surface, and equal, approximately, to one atmosphere, (3) the temperature of the gas and of the solid must be the same, and must be known.

The satisfaction of these three conditions was ensured by the construction of the furnace and of the sample assembly. The sample was exposed to the action of carbon dioxide flowing through a tube furnace packed with refractory at the inlet end so that the gas would reach the temperature of the furnace. The samples were short annular pieces of graphite (A in Fig. 1) whose outer surfaces were machined and polished to the same diameter as the two-part stream-lined Sillimanite holders, B and C. When a sample was inserted in the holder and the cracks between its edges and the shoulders of the holder carefully luted with refractory cement, only the measured cylindrical surface was exposed to the action of the atmosphere. The shape of the holder ensured approximately laminar flow past the sample so that the pressure of the gas over the entire sample surface was the static pressure at that point. This was tapped off by the silica tube, D. The temperatures were measured by means of thermocouples, E_1, recessed into the sample, and E_2, in the gas stream.

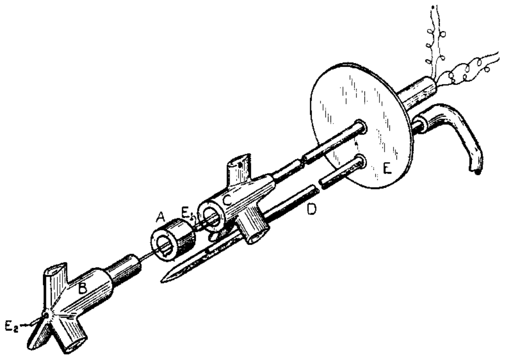

Fig. 1.—Sample assembly: A, sample; B, C, sillimanite sample holder; D, pressure tap; E_1, E_2, thermocouple junctions; E, brass end-plate.

(4) The concentration of the reacting gases *at the sample surface* must be known.

This condition is most easily satisfied by making the composition of the gas in contact with the sample as nearly as possible 100% carbon dioxide. To do this, concentration gradients in the vicinity of the sample must be eliminated. Consider the partial pressures of the gaseous components of a heterogeneous reaction in the neighborhood of the reacting surface when the rate of reaction is determined, at least partly, by rates of diffusion. This condition is represented graphically in Fig. 2, in which the abscissas represent radial distances from the reacting surface, and the ordinates partial pressures of the gaseous constituents. P is the partial pressure of the reacting gas, and p that of the

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(1) (a) Broom and Travers, *Proc. Roy. Soc.* (London) **A135**, 512 (1932); (b) Drakeley, *J. Soc. Chem. Ind.*, **50**, 219T (1931); (c) Key and Cobb, *J. Soc. Chem. Ind.*, **49**, 439T, 454T (1930); (d) Jones, King and Sinnatt, Dept. Sci. Ind. Research Brit. Tech. Paper Fuel Research No. 18 (1927); (e) Agde and Schmitt, *Z. angew. Chem.*, **40**, 1003, 1027 (1927).

product of reaction, in the region far from the surface; while the same letters, primed, represent the values of these quantities at the surface. Then P' is fixed by the equality of the rate at which the surface reaction occurs at this pressure with the rate at which the reacting gas can diffuse to the surface from the partial pressure P at an infinite distance. Thus, if the rate of reaction at unit pressure is σ, and if, as has been shown to be true for the reduction of carbon dioxide by carbon[1b,c,2] the reaction is of the first order, then

$$A_{\text{obs.}} = \sigma P' = \int_{\lambda} \left(-D \frac{\partial p}{\partial x} \right) d\lambda \qquad (1)$$

where $A_{\text{obs.}}$ is the observed rate of reduction at velocity considered; D is the coefficient of diffusion and λ is the surface through which diffusion occurs. It will be shown in a later paper that the integral in the right-hand side of this equation is a continuously increasing function of the velocity of gas flow. Then as the gas velocity increases P' must increase to maintain the equality in Equation (1); and the partial pressures take on successively the values represented by the dotted lines a, b in Fig. 2, until, in the limit, $P' = P$, when $A_{\text{obs.}} = A$.

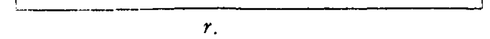

Fig. 2.—Concentrations of the gases near a reacting surface.

Hence the fourth condition was satisfied by observing the rate of formation of carbon monoxide at any temperature with increasing rates of gas flow past the sample, until a further increase in gas velocity caused no further increase in the rate of formation of carbon monoxide. Then the partial pressure of carbon dioxide in contact with the reacting surface was only infinitesimally different from that at a distance from it. Since this condition was secured only when the concentration of carbon monoxide in the off gases was very small (less than 1 to 20 parts of carbon monoxide in a thousand of carbon dioxide), the partial pressure of the carbon dioxide was practically equal to the total pressure.

Apparatus and Materials

The samples used in these experiments were machined from cylindrical graphite electrodes of the spectroscopic grade supplied by the Acheson Graphite Co. The outside diameter of the finished samples was 21.3 mm., while the length was about 14 mm. The surfaces were finished by polishing with graphite to secure initial uniformity of all samples.

The sample assembly, described above (Fig. 1), hung from the thermocouple protecting tube, which was cemented into a copper tube in the end-plate of the water-cooled exit end bell of the furnace. The pressure tap, which was connected by rubber tubing with a U-tube containing oil of specific gravity 0.86, was cemented into another copper tube in the same plate. This plate and the one for the inlet end of the furnace were fastened to their respective end bells by knurled brass nuts. The end bells were annular brass boxes arranged for water cooling and were cemented to the ends of the Sillimanite furnace tube, which was 122 cm. long and had an inside diameter of 5.1 cm. The furnace was heated electrically by cascaded nichrome and platinum windings.

Temperatures were measured by thermocouples of platinum–5% rhodium *vs.* platinum–20% rhodium wire 0.64 mm. diameter. These alloys and the heavy gage wire were chosen to minimize the effect of the deterioration of platinum by carbon monoxide at high temperatures. The couples were calibrated throughout the range before the series against a standardized platinum *vs.* platinum–10% rhodium couple. After run No. 133 the thermocouples failed near the hot junction. The junction was rewelded and the thermocouple recalibrated. There was no change in calibration. When the sample was in place, couple E_1 (Fig. 1) gave readings 10–50° lower than E_2, although previous exploration had showed uniform temperatures in that part of the furnace. When couple E_1 was made of smaller wire, which could be used at lower temperatures, these differences disappeared. Hence it was concluded that the differences were due to thermal conduction along the heavy wire and that the temperatures of both gas and sample were given with sufficient accuracy by couple E_2.

The gas supply train consisted of a tank of commercial carbon dioxide which discharged to a large purifying tube containing copper and copper oxide maintained at 650°, followed by a large drying tube containing Anhydrone (anhydrous magnesium perchlorate). The carbon dioxide was measured by one of three interchangeable flow meters, read to 0.04 mm. in a deflection of 10 to 50 mm. by means of a Starrett depth gage, and then passed to the furnace. The flowmeters, whose ranges were 0.6–2.0, 1–5 and 5–20 liters per minute, were calibrated against a standard wet test meter.

The off gas from the furnace was collected in a gasometer, sealed with dry glycerol, of about 80 liters capacity, from which it was discharged at a rate of about 1 liter per minute, through the analysis apparatus. The difficulties of analyzing the large volumes of gas for small concentrations of carbon monoxide were met by using a modified iodine

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(2) Rhead and Wheeler, *J. Chem. Soc.*, **101**, 631 (1912).

pentoxide method.[3] The apparatus (Fig. 3) consisted of a trap A, cooled by solid carbon dioxide in trichloroethylene to remove any condensable materials, a reaction tube B containing about 600 g. of iodine pentoxide, maintained at a temperature of 160 ± 10° by an electrically heated air-bath, and a delivery tube C, heated to prevent the condensation of iodine, to which was connected by a ground-glass joint the V tube condenser D, packed with Pyrex glass beads and cooled by solid carbon dioxide in trichloroethylene. The gas to be analyzed was drawn through this apparatus by an aspirator controlled by the suction regulator E, and the whole apparatus could be swept with commercial nitrogen drawn through the mercury check valve F. After a run, the V tube D was removed and washed with 10% potassium iodide solution and distilled water and the iodine titrated with sodium thiosulfate solution, using starch as indicator. This apparatus was checked a number of times with synthetic carbon monoxide–carbon dioxide mixtures. Carbon monoxide determined by analysis agreed within 2% with the measured amount admitted to the apparatus up to flow rates of 1.3 liters per minute.

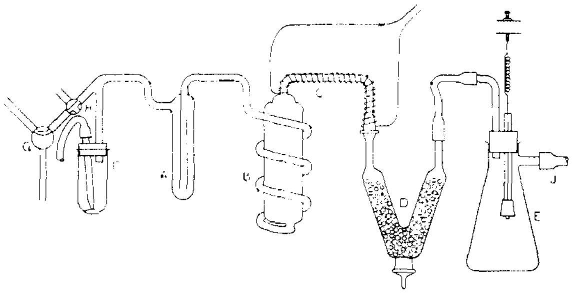

Fig. 3.—Diagrammatic layout of gas analysis apparatus: A, drying trap (cooling bath not shown); B, iodine pentoxide tube (heating bath not shown); C, delivery tube; D, iodine condenser (cooling bath not shown); E, suction regulator; F, check valve in nitrogen line; G, three-way stopcock to furnace and gasometer; H, three-way stopcock to waste; J, to aspirator.

Procedure

A standard procedure was developed and tested in the first eighty runs. The furnace was brought to the temperature at which succeeding runs were to be made and the holder, without a sample, was placed in it. Several blank runs were made and the sample holder was then removed, cooled, and a measured sample inserted. The assembly was replaced in the furnace and a run was started as soon as the sample reached a constant temperature as indicated by thermocouple E_1. Runs were made as frequently as possible after that, about one every hour, until the data showed that the sample had been consumed so far that, with the holder, it no longer exposed a smooth surface to the flow of gas. Before starting any run the analysis apparatus was swept with nitrogen for ten minutes, and the furnace with carbon dioxide for five minutes at the gas flow rate to be used in the following run. At time zero the furnace was connected with the gasometer. Readings of the flowmeter, temperatures and gas pressures were taken three to five times during each run, which usually lasted five minutes, though at low flow rates they were sometimes extended to ten minutes, while at high gas velocities three-minute runs filled the gasometer. The nitrogen sweeping of the analysis apparatus continued through this part of the run to prevent accumulation of iodine. At the end of the run, the furnace gases were again discharged to waste, a clean, carefully dried V-tube[4] was inserted in the analysis apparatus and the gas drawn through it from the gasometer. The analyzer was swept with nitrogen again for five minutes after the gasometer was emptied, after which the V-tube was removed and washed, and the wash solution titrated. The log of a typical run is given in Table I.

TABLE I

LOG OF RUN NO. 128

May 10, 1933; barometer 736.3; rm. temp. 24.2°

Notes	Time, min.	CO_2 flow-meter def., mm.	Temperatures, °C.		Pressures	
			Gas, mv.	Sample, mv.	F. M. mm. Oil	S mm. Oil
N_2 on analyzer	−10					
CO_2 on furnace	− 5					
CO_2 to gasometer	0.00	39.04	7.55	7.03	120	26
	2 1/2	39.70	7.55	7.03	120	26
CO_2 to waste	4.25	38.82				
Fresh condenser on analyzer	6.5					
Gasometer discharge to analyzer	7.5					
Gasometer empty	44.0					
N_2 off; condenser removed	49.0					
Averages		39.2	7.55	7.03	120	26
Average values						
CO_2 flow liters/min.		12.8				
Temperatures, °C.			1146	1099		
Pressures, mm. Hg					7.5	1.6

Titration of iodine, ml.

Rdg. 2	42.46	1 ml. = 7.48 cc.
Rdg. 1	0.64	CO at N. T. P.
Diff.	41.82	
Blank	0.93	
	40.89	

Equivalent CO 305.9 cc.

Results

In selecting results for calculation only those runs which were in error because of changing furnace temperature during the run, loss of iodine in washing out the condenser, or inaccurate titration, were rejected. The results of all other determinations of the rate of reduction of carbon dioxide by graphite are given in Table II. The first four columns of this table are self-explanatory. The fifth column gives the rate

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[3] Vandaveer and Gregg, *Ind. Eng. Chem., Anal. Ed.*, **1**, 129 (1929); Emmett and Shultz, THIS JOURNAL, **52**, 1782 (1930).

[4] The V-tubes were dried between runs in a drying oven at 110° for two hours, and then cooled by aspirating dry air through them for twenty minutes. This drying was imperative as it was found that small amounts of water took up enough carbon dioxide at the low condenser temperature to attack the soft glass beads used at first. This permitted the accumulation of finely divided silica which appeared to be capable of taking up iodine, thus vitiating the analysis. This difficulty was eliminated by careful drying and the use of Pyrex glass beads.

of formation of carbon monoxide, measured in cubic millimeters at N. T. P. per sq. cm. per second, observed at the actual pressure in the furnace (column 4). In the sixth column these values are corrected to standard atmospheric pressure, assuming the reaction to be of the first order.[1b,c,2] These data permitted the determination of approximate temperature coefficients so that the values of rate in each temperature group could be corrected to a standard temperature. From plots of these corrected values against gas flow rate, as in Figs. 4 and 5, it was possible to select the runs in the region of zero velocity coefficient, *e. g.*, those at rates above 5 liters per minute at 965° (Fig. 4), and those above 6 liters per minute at 1145° (Fig. 5).

TABLE II

RATES OF FORMATION OF CARBON MONOXIDE AT VARIOUS TEMPERATURES AND GAS VELOCITIES

Run	Temp., °C.	Gas velocity, liters at N. T. P. per minute	Press. at Sample, mm.	Rate of formation of CO Obs. cu. mm. at N. T. P. per cm.² per sec.	Rate of formation of CO Corr. to 760 mm. cu. mm. at N. T. P. per cm.² per sec.
			1300°		
134	1303	16.7	793	518	495
131	1306	12.4	741.8	502	513
			1150°		
127	1144	11.7	738.7	122	126
128	1146	11.1	737.9	127	131
123	1147	9.7	741.1	131	134
125	1153	9.4	741.5	128	131
124	1151	6.3	741.9	136	139
126	1154	4.5	740.6	95	97
			1000°		
112	1001	4.11	727.4	24.5	25.3
110	999	2.63	727.7	21.6	22.8
111	1002	2.59	727.1	22.1	23.1
113	1001	2.19	726.3	18.0	18.9
114	999	1.07	725.5	9.4	9.9
			960°		
152	969	11.3	748.1	18.9	19.2
135	952	6.2	737.7	13.8	14.2
136	958	5.5	736.7	15.3	15.8
137	980	5.2	736.0	16.7	17.2
138	979	6.6	737.3	25.2	26.0
153	961	4.90	742.8	17.5	17.9
151	984	4.22	744.3	20.6	21.1
154	964	3.72	739.1	11.3	11.7
155	967	3.60	739.6	14.3	14.7
156	968	3.36	738.4	14.6	15.1
159	973	3.85	737.4	14.1	14.5
95	942	1.16	739.4	3.5	3.6
96	940	1.11	728.3	2.9	3.0
97	950	1.10	728.1	3.4	3.6
98	955	1.07	727.9	3.4	3.5
157	971	0.72	738.1	6.0	6.2
			920°		
171[a]	907	12.3	751.7	2.75	2.78
170[a]	920	8.1	746.0	2.82	2.87
172[a]	916	6.8	746.8	2.70	2.75
173[a]	916	7.0	747.6	2.67	2.71
174[a]	917	6.9	748.3	2.60	2.64
175[a]	914	7.1	749.2	2.08	2.11
169	925	3.61	743.4	1.55	1.59
			875°		
164	876	8.6	741.8	2.07	2.12
160	883	3.36	739.5	1.75	1.80
161	876	3.38	739.6	1.73	1.78
162	882	3.56	739.9	1.63	1.67
163	884	1.94	739.6	0.55	0.56
			850°		
149	850	12.8	749.0	1.17	1.19
140	856	6.1	738.0	1.35	1.39
141	859	5.6	737.6	1.48	1.53
147	848	5.3	740.0	1.10	1.13
148	850	4.7	739.9	1.46	1.18
82	857	1.07	746.1	0.76	0.77
145[b]	860	6.3	741.9	.71	.73
150[b]	853	5.7	743.7	.81	.83
143[b]	864	2.61	740.4	.47	.48
142[b]	864	2.64	740.3	.28	.27
144[b]	862	0.83	740.3	.23	.24

[a] These runs were taken after various intervals in the furnace (see Table III).

[b] These runs were taken after twenty-four hours in the furnace.

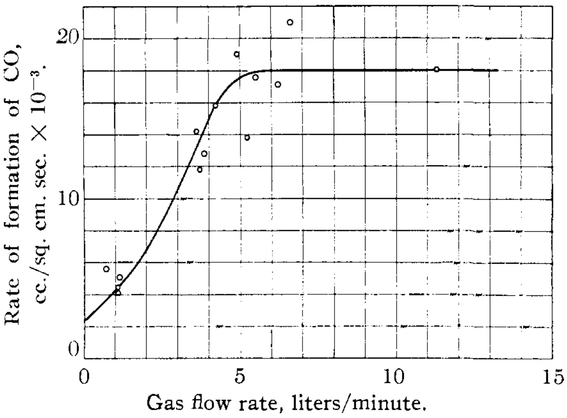

Fig. 4.—Variation of rate of formation of carbon monoxide with gas velocity at 965°. The two points at (5.3, 12.8) and (6.6, 21) were rejected since their deviations from Equation (3) were more than 3σ.

In this way twenty-four points satisfying the criteria set out in the first part of this paper were obtained from which to compute the values and the standard deviations of the constants E and b in the Arrhenius equation

$$\log A = -(E/4.575\ T) + b \qquad (2)$$

where A is the rate of formation of carbon dioxide, cc./sq. cm./sec.; T the absolute temperature, degrees C.; E and b are constants. In calculating these constants the values in the last column of Table II were used, not the values corrected to standard temperatures used to determine the region of zero velocity coefficient.

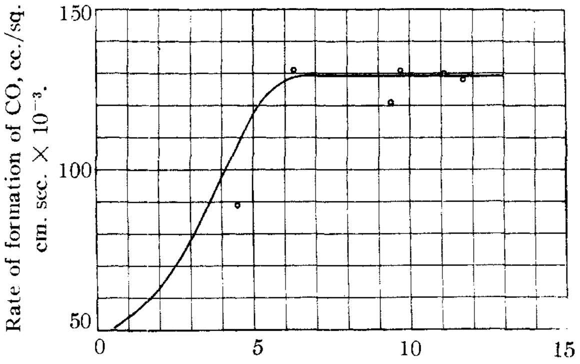

Fig. 5.—Variation of rate of formation of carbon monoxide with gas velocity at 1145°.

These points fell into two groups, fourteen in the high temperature range, above 950°, and ten in the low temperature range, from 850 to 950°, when plotted as circles in Fig. 6, where the abscissas represent the inverse absolute temperatures, and the ordinates, log A. The solid lines represent the correlating equations given below. The appearance of a sudden increase in reactivity of cokes at about 1000°, which corresponds to the transition from the low temperature to the high temperature reactions of this paper, has been noted recently by T. Namikawa.[5]

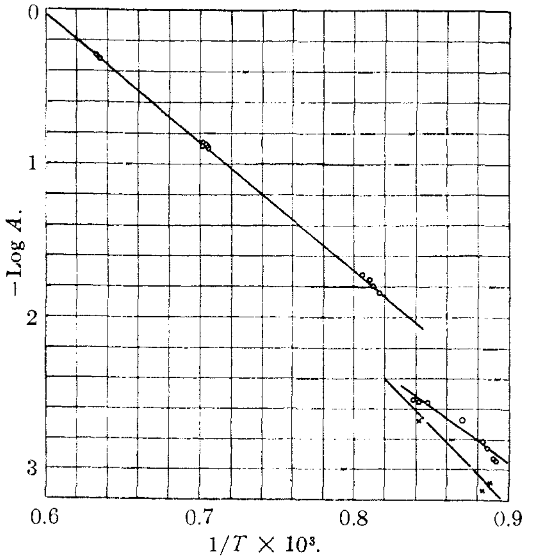

Fig. 6.—Rate of formation of carbon monoxide at various temperatures.

Two of the points in the high temperature range were found to have deviations about 3.5 times the standard. When the constants were recomputed omitting these two points, the result was

$$\log A_1 = 5.07 \pm 0.04 - (38{,}700 \pm 8)/4.575\,T \quad (3)$$

for the range 950° to 1300°. The ten low temperature points (850–950°) are correlated by the equation

$$\log A_2 = 3.40 \pm 0.34 - (32{,}360 \pm 60)/4.575\,T \quad (4)$$

The deviations given above correspond to standard deviations of individual points from the correlating curves (1) in the high temperature range, of ± 0.0129 in log A_1 or $\pm 3\%$; and (2) in the low temperature range, of ± 0.0275 in log A_2 or $\pm 6.5\%$. It is not claimed that these values are an indication of the absolute accuracy of the work, but rather of its internal consistency. An estimate of the accuracy of the determinations may be made. The most probable source of error is in the temperature measurement, though this is believed to be correct within 5°. The consistency of the data indicates that any error in temperature measurement must vary regularly throughout the range. If, then, it is assumed that the temperature as measured is 10° high at 1300° and 5° high at 950°, the constants in the equation for A_1 become $b = 5.14$ and $E = 38{,}880$. A constant error in temperature measurement makes no appreciable difference in the values of the constants, so the low temperature correlation, since it covers only a small range of temperature, may be considered correct. As the calculation above shows, an error of 200 calories in E may be considered possible for the high temperature range.

Discussion

While equations of the type of the correlating equations are, strictly speaking, empirical formulas, their constants are usually considered to have theoretical significance. The quantity E, which has the dimensions of energy, may be thought of as an energy of activation. Hence it will, presumably, vary only with the degree of chemical unsaturation of the surface atoms of the solid. The constant b, whose magnitude depends on the units used, is a function of physical

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(5) T. Namikawa, *J. Soc. Chem. Ind. Japan*, **36**, Suppl. binding, 242 (1933); *C. A.*, **27**, 3583 (1933).

factors such as the gas pressure, the microscopic development of the surface, and the condition and magnitude of the adsorbed film. In the case under consideration, the discontinuity at 950° results from a considerable change in b. Since it is hardly likely that any great change in the physical condition of the solid occurs at this temperature, and the pressure of the gas remains constant, the change in b may be due to a decrease in the extent of the adsorbed film, leaving a larger proportion of the solid surface available for reaction.

The appearance of two separate processes may throw some additional light on the nature of the solid carbon-oxygen complex postulated by previous workers[1a,6] on the oxidation of solid carbon. Broom and Travers[1a] and Langmuir[7] found that when carbon dioxide reacted with carbon at low temperatures ($T < 1250$°K.) carbon monoxide was formed at the same rate as that at which carbon dioxide disappeared. This is explained by the retention of half of the oxygen of the carbon dioxide by the graphite. This reaction

$$C + CO_2 \longrightarrow CO + C{-}O_{solid}$$

with a small contribution to the rate of formation of monoxide due to the slow decomposition of the solid complex, probably is the one whose speed determines the rate measured in the low temperature range. The chemical nature of the material represented by $C{-}O_{solid}$ is not yet clear. It may be adsorbed[6e] or dissolved oxygen[6a,b,c] or adsorbed carbon monoxide.[1a] Whatever its nature, it presumably hinders further oxidation in the places where it occurs, and is removed only by its decomposition, at a characteristic rate determined by the temperature, into the two gaseous oxides. If this is the case, (1) a sample subjected to oxidation at low temperature for a long time should eventually be entirely covered with a layer of this oxide, when the observed reactivity would be less than with a fresh sample, and fixed by the rate of decomposition of the complex; and (2), if the temperature coefficient of the decomposition of the oxide were greater than that of its formation, a temperature would be reached above which the surface complex decomposes as rapidly as it is formed, leaving a clean surface for reaction.

TABLE III

EFFECT OF LENGTH OF EXPOSURE ON REACTIVITY AT LOW TEMPERATURES

Time, hrs.	Run	Temp., °C.	Gas velocity l./min.	Formation of CO Cu. mm. per sq. cm. per sec.	Formation of CO Corr. cu. mm. per sq. cm. per sec.
At 850°					
2.9	140	856	6.1	1.39	1.26
3.3	147	848	5.3	1.13	1.17
4.1	141	859	5.6	1.53	1.32
4.8	148	850	5.5	1.18	1.18
5.7	149	850	14.6	1.19	1.19
23.7	150	853	5.7	0.83	0.79
25.0	145	860	6.3	.73	.62
At 925°					
0.42	169	925	3.61	1.59	1.44
1.42	170	920	7.0	2.87	2.74
3.17	171	907	12.2	2.78	3.06
4.73	172	916	6.8	2.75	2.75
6.92	173	916	7.0	2.71	2.71
9.67	174	917	6.9	2.64	2.60
15.75	175	914	7.1	2.11	2.18

The first consequence of this hypothesis was tested at about 850° and at about 925°. The data are given in Table III. The last column in this table was obtained by correcting the observed values to standard temperatures by means of the temperature coefficient of Equation (4). In the test at 850° the sample was not appreciably reduced in size after twenty-four hours, and the lowered rate of formation of carbon monoxide was fairly reproducible. The test at 925° was not quite satisfactory, as the sample was consumed too rapidly. When, however, the two points at 850° after twenty-three hours, and the one at 925° after fifteen hours are plotted (as crosses in Fig. 6), they indicate a process (the dotted line in Fig. 6) whose temperature coefficient is considerably greater than that of the rate measured on a fresh sample.

Evidently, somewhere between 925 and 950° the velocity of this decomposition reaction becomes great enough to clean up the surface as fast as it is covered. The fact that, at this temperature, the rate of formation of carbon monoxide by the decomposition reaction is very nearly as great as that of the usual reduction of carbon dioxide indicates the possibility that, contrary to what has been found at higher temperatures,[6a,b] the sole product of this decomposition may be carbon monoxide. Then it is to be expected, as is found

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(6) (a) L. Meyer, *Z. physik. Chem.*, **B17**, 385 (1932); (b) V. Sihvonen, *Ann. Acad. Sci. Fennicae*, **A34**, No. 7 (1932); (c) A. Eucken, *Z. angew. Chem.*, **43**, 986 (1930); (d) Lowry and Hulett, THIS JOURNAL, **42**, 1408 (1920); (e) Rhead and Wheeler, *J. Chem. Soc.*, **103**, 461, 1210 (1913).

(7) Langmuir, THIS JOURNAL, **37**, 1139 (1915).

to be the case, that the high temperature rate, A_1, in the neighborhood of the transition point, would differ from the low temperature rate, A_2, by a factor somewhat greater than 2. For if all the oxygen in the carbon dioxide that reacts goes to the monoxide, the high temperature rate must be represented by

$$C + CO_2 \longrightarrow 2CO$$

from which the factor 2 arises. In addition, since the carbon surface is cleaned up by the increased rate of decomposition, an increased rate of reaction is to be expected due to the increased availability of active surface. The latter consideration also accounts for the increased temperature coefficient, since the average energy of the surface available for reaction would be increased by the loss of the solid oxide, which was, presumably, most stable on the least saturated portions of the surface. Thus the high temperature rate A_1 may perhaps be represented by

$$C + CO_2 \longrightarrow CO + C\text{—}O_{\text{solid}}$$
$$C\text{—}O_{\text{solid}} \longrightarrow CO$$

where the second reaction follows so rapidly on the first that there is no accumulation of the solid oxide.

Summary

1. The measurement of the rate of a rapid heterogeneous reaction which usually is governed by diffusion conditions has been considered from a theoretical viewpoint. This discussion led to the development of a method which was used to determine the rate of reduction of carbon dioxide by graphite. The method involves the elimination of concentration gradients by increasing the gas velocity across the reacting surface until the velocity coefficient of the observed rate of reaction vanishes.

2. The rate of reduction of carbon dioxide has been measured in terms of cubic centimeters of carbon monoxide at N. T. P. produced per second from carbon dioxide at one atmosphere in contact with one square centimeter of graphite surface. It is given, for temperatures between 950 and 1300°, by the equation

$$\log A_1 = 5.07 - (38{,}700/4.575\ T)$$

and for temperatures between 850 and 950°, by

$$\log A_2 = 3.40 - (32{,}360/4.575\ T)$$

3. The significance of the appearance of two stages in the oxidation of graphite by carbon dioxide and its relation to the surface oxide complex are discussed.

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The Solubility of Hydrogen in Water at 0, 50, 75 and 100° from 25 to 1000 Atmospheres

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This is a continuation of previous work.[1] The apparatus and method have been described. The hydrogen was 99.9 per cent. pure, the impurity being nitrogen. A correction was applied assuming that the amount of nitrogen dissolved was proportional to its mole fraction. Table I gives a summary of the experimental results; the previously published[1] values for the 25° isotherm are added for comparison. Figure 1 shows a plot of the results. A correction for the change of vapor pressure due to the gas pressure on the liquid was made in the manner already explained.[1] Table II shows values of the vapor pressure of water at 100° used in making this correction. These values are only approximate, but a relatively large error in the partial pressure of water will make only a small correction in the final results. The total experimental error amounts to a few tenths of a per cent.

By a sensitive method of plotting deviations, the experimental data were smoothed with respect to both pressure and temperature to obtain interpolated solubility values. The results obtained by such interpolation are given in Table III. It was thought that an extrapolation of the results at 25 atmospheres to lower pressures by means of Henry's law, when corrected for deviations from the perfect gas law, would yield fairly accurate values for the absorption coefficient at one atmosphere. The following table gives the extrapolated values in terms of the Bunsen and Ostwald absorption coefficients[2] and shows also

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(1) Wiebe, Gaddy and Heins, *Ind. Eng. Chem.*, **24**, 823, 927 (1932); THIS JOURNAL, **55**, 947 (1933).

(2) For definitions see "I. C. T.," Vol. III, pp. 254–255.