

CARBON DIOXIDE-COKE REACTIONS

Experimental Procedure and Results

The experiments were conducted in small fluidized beds under isothermal conditions to minimize the influence of rates of thermal-energy transfer upon the overall rates. The apparatus is shown in figure 1. The reaction tube, 2.22 cm. inside diameter and 56 cm. long, was made of a high-temperature porcelain. The tube was held vertically in a furnace, the heated chamber of which was a prismatic cavity of 11.5 by 11.5 by 23.0 cm. The furnace was

heated by four silicon carbide heating elements. Standard tapered Pyrex²⁶ joints were fused to both ends of the reaction tube to eliminate high-temperature seals and permit flexibility in operation. The temperature was measured with a Pt-Pt+10 pct. Rh thermocouple placed vertically in the tube from the top. During a run the position of the thermocouple was changed radially and vertically to assure that isothermal conditions were maintained. The rates of flow of gas were measured by means of capillary flowmeters (fig. 2). Flow measure-

²⁶ Reference to specific brands is made to facilitate understanding and does not imply indorsement of such items by the Bureau of Mines.

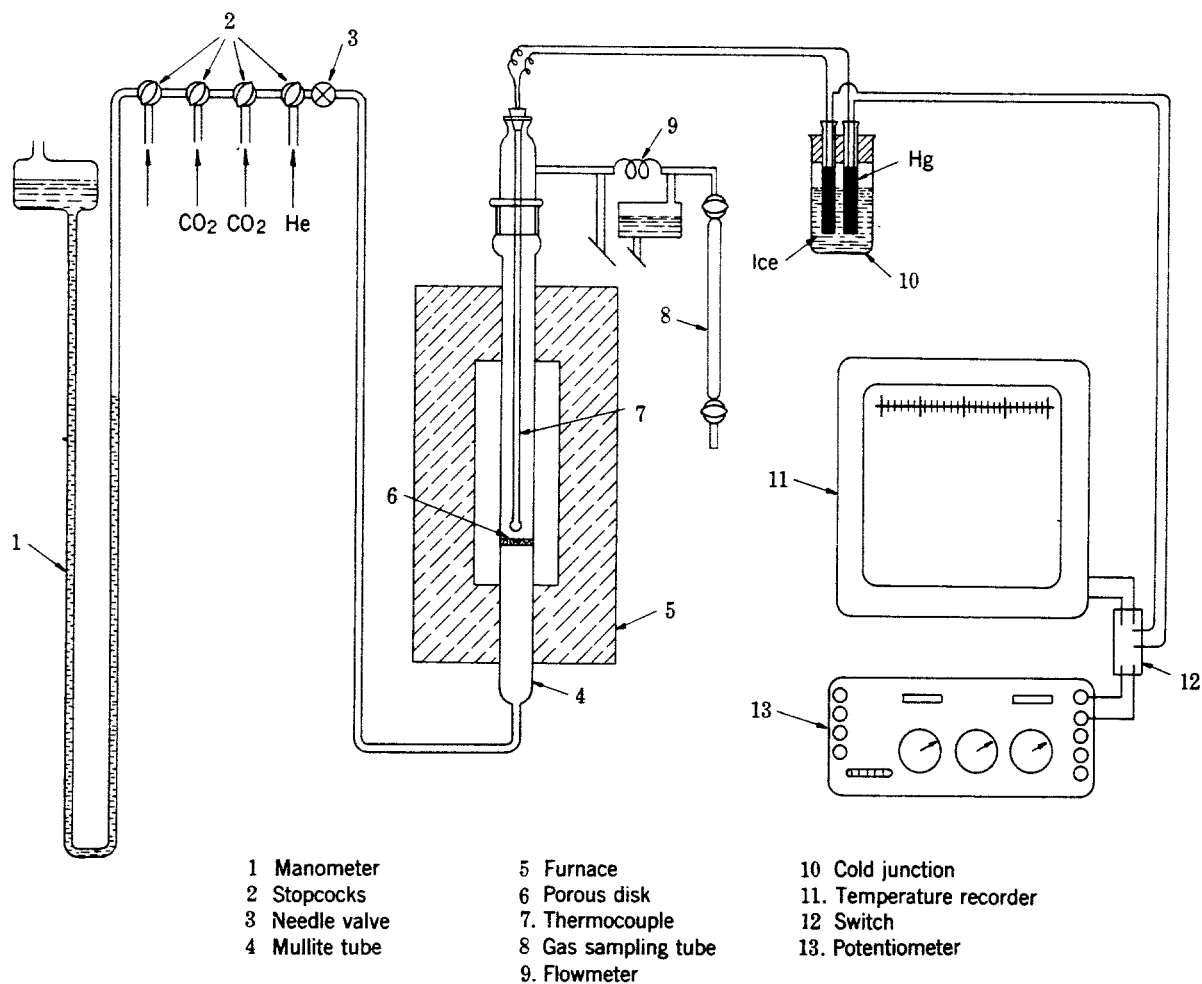


FIGURE 1.—Apparatus.

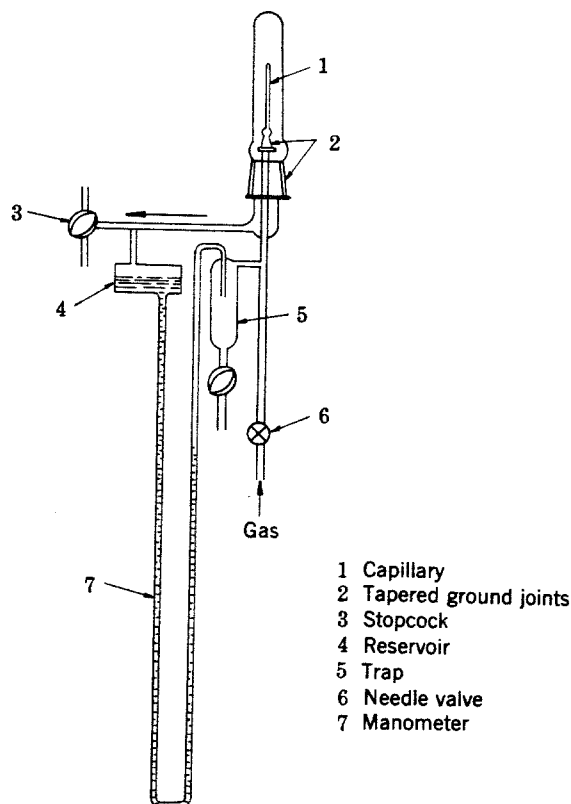


FIGURE 2.—Gas Flowmeter.

ments were always made at constant absolute downstream pressures.

The coke used in this study was a foundry coke (900° C.) and contained 7.4 pct. ash. Closely screened and weighed amounts of coke, ranging from 8–16 to 100–140 mesh U.S. standard, were introduced from the top by removing the upper half of the tapered joint. Product gases were passed through a capillary flowmeter and sampling tubes. When the temperature of the bed and exit gas flow rate assumed constant levels, that is, steady state, gas samples were taken for analysis. The loss in weight of the coke sample, that is, burn off, usually was kept below 5 pct.; the loss was calculated from the rate and composition of the effluent gas and the time elapsed to reach steady state. Corrections were made in the weight of the sample for the amount of burn off at the time of gas sampling. When a run was completed, the sample was removed by suction through a 6-mm. porcelain tube inserted into the reaction tube.

The aerodynamic surface area and density of the coke samples were determined, by methods previously described,^{27, 28} in order to estimate rates necessary for fluidization.²⁹ Ap-

proximate rates of gasification were then obtained. Mixing in the gas phase was generally studied by gasifying at successively increased rates of flow of carbon dioxide and with increased amounts of coke, while a constant ratio of weight of carbon to rate of flow of carbon dioxide was maintained. The most precise experimental values for the rate constants were obtained under conditions of either negligible mixing or thorough mixing; however, these conditions could not always be realized, owing to the fact that experiments in fluidized beds can be carried out only over a limited range of flow rates. This range, between incidence of fluidization and bubble or slug formation, covers approximately a twofold flow rate.

Final gasification runs were conducted at constant rates of flow of carbon dioxide with successively increased amounts of carbon, for example 1 to 7 g. Helium or nitrogen was used to flush the system and also to serve as a tracer in the experiments, that is, to check the material balance of the reaction. The rate of flow of inert gas was about one-tenth that of carbon dioxide. The experimental results are shown in tables 1 and 2.

TABLE 1.—Reaction of carbon dioxide with a high-temperature metallurgical coke

Run No.	Weight of carbon, grams	Inlet CO ₂ rate ¹	He rate ¹	Outlet (CO)/(CO ₂) ¹
Temperature 900° C.; Particle Size 8–100 Mesh (U.S. Standard)				
351.....	1.68	2.51	0.186	0.022
352.....	3.36	2.51	.186	.037
353.....	3.36	1.50	.379	.053
Temperature 900° C.; Particle Size 100–140 Mesh (U.S. Standard)				
354.....	3.36	1.06	0.379	0.077
355.....	3.36	.83	.379	.098
356.....	4.0	.74	.379	.116
357.....	4.0	.60	.57	.132
358.....	4.0	.495	.57	.152
359.....	4.2	.446	.57	.156
360.....	4.8	.446	.57	.185
361.....	5.4	.446	.57	.200
362.....	6.0	.446	.57	.213
Temperature 950° C.; Particle Size 100–140 Mesh (U.S. Standard)				
339.....	1.68	2.49	0.186	0.073
340.....	3.36	2.49	.186	.112
341.....	3.36	1.50	.379	.168
342.....	3.36	1.05	.379	.212
343.....	3.36	.83	.379	.249
344.....	4.0	.74	.379	.302
345.....	4.0	.80	.57	.327
346.....	4.0	.493	.57	.384
347.....	4.2	.446	.57	.425
348.....	4.8	.446	.57	.483
349.....	5.4	.446	.57	.57
350.....	6.0	.446	.57	.62

See footnote at end of table.

²⁷ Ergun, S., Determination of Geometric Surface Area of Crushed Porous Solids-Gas Flow Method: Anal. Chem., vol. 24, 1952, pp. 388–393.

²⁸ Work cited in footnote 23, p. 5.

²⁹ Ergun, S., Determination of Particle Density of Crushed Porous Solids: Anal. Chem., vol. 23, 1951, pp. 151–156.

TABLE 1.—Reaction of carbon dioxide with a high-temperature metallurgical coke—Continued

Run No.	Weight of carbon, grams	Inlet CO ₂ rate ¹	He rate ¹	Outlet (CO)/(CO ₂) ¹
Temperature 1,000° C.; Particle Size 80-100 Mesh (U.S. Standard)				
296.....	1.68	2.49	0.379	0.163
297.....	2.24	2.49	.379	.210
298.....	2.80	2.49	.379	.253
299.....	3.36	2.49	.379	.291
300.....	3.36	2.13	.379	.324
301.....	3.36	1.88	.379	.346
302.....	3.36	1.66	.379	.387
303.....	3.36	1.50	.379	.407
304.....	3.36	1.25	.379	.442
305.....	4.48	1.25	.379	.60
306.....	5.60	1.25	.379	.75
307.....	6.72	1.25	.379	.79
Temperature 1,000° C.; Particle Size 100-140 Mesh (U.S. Standard)				
308.....	4.20	0.62	0.57	1.12
309.....	5.04	.62	.57	1.20
310.....	5.88	.62	.57	1.30
311.....	6.72	.62	.57	1.43
312.....	4.00	.59	.57	.96
313.....	4.00	.426	.57	1.16
314.....	4.00	.323	.57	1.58
315.....	4.00	.253	.57	1.94
Temperature 1,050° C.; Particle Size 80-100 Mesh (U.S. Standard)				
316.....	1.12	2.51	0.186	0.186
317.....	1.68	2.51	.186	.268
318.....	2.24	2.51	.186	.337
319.....	3.36	2.51	.186	.448
320.....	3.36	2.51	.186	.458
321.....	3.36	1.88	.186	.54
322.....	3.36	1.50	.379	.66
323.....	3.36	1.25	.379	.80
324.....	3.36	1.06	.379	.79
325.....	3.36	.93	.379	1.26
326.....	3.36	.83	.379	.97
Temperature 1,050° C.; Particle Size 100-140 Mesh (U.S. Standard)				
327.....	4.0	0.89	0.57	1.40
328.....	4.0	.81	.57	1.57
329.....	4.0	.74	.57	1.70
330.....	4.0	.69	.57	1.73
331.....	4.0	.64	.57	1.81
332.....	4.0	.60	.57	1.88
333.....	4.0	.56	.57	2.02
334.....	4.0	.52	.57	1.89
335.....	4.0	.495	.57	2.09
336.....	4.0	.446	.57	2.25
337.....	5.0	.446	.57	2.84
338.....	6.0	.446	.57	3.48
Temperature 1,080° C.; Particle Size 80-100 Mesh (U.S. Standard)				
Run No.	Weight of carbon, grams	Inlet CO ₂ rate ¹	He rate ¹	Outlet (CO)/(CO ₂) ¹
231.....	1.2	2.49		0.306
232.....	2.0	2.49		.444
233.....	2.8	2.49		.56
234.....	4.2	2.49		.87
235.....	5.6	2.49		.98
236.....	7.0	2.49		1.31
237.....	4.2	2.49		.74
238.....	4.9	2.49		.96
239.....	5.6	2.49		1.17
240.....	6.3	1.28		2.07
241.....	7.0	1.28		2.50
242.....	7.7	1.28		2.86
243.....	4.2	1.28		1.48
244.....	4.9	1.28		1.73
245.....	5.6	1.28		2.05
246.....	3.5	1.28		1.33
247.....	4.9	1.28		1.73
248.....	6.3	1.28		2.47

See footnote at end of table.

TABLE 1.—Reaction of carbon dioxide with a high-temperature metallurgical coke—Continued

Run No.	Weight of carbon, grams	Inlet CO ₂ rate ¹	He rate ¹	Outlet (CO)/(CO ₂) ¹	
Temperature 1,150° C.; Particle Size 80-100 Mesh (U.S. Standard)					
363.....	1.12	2.49	0.186	0.57	
364.....	1.68	2.49	.186	.84	
365.....	2.24	2.49	.186	1.00	
366.....	2.24	2.49	.186	1.08	
367.....	3.36	2.49	.186	1.58	
368.....	3.36	1.88	.186	2.20	
369.....	3.36	1.88	.186	2.22	
370.....	3.36	1.50	.379	2.98	
371.....	3.36	1.25	.379	3.37	
372.....	3.36	1.25	.379	3.38	
373.....	3.36	1.05	.379	3.77	
374.....	3.36	.93	.379	4.20	
375.....	3.36	.93	.379	5.40	
376.....	3.36	.88	.379	4.50	
Temperature 1,150° C.; Particle Size 100-140 Mesh (U.S. Standard)					
377.....	4.0	0.89	0.379	7.2	
378.....	4.0	.89	.379	7.3	
379.....	4.0	.81	.57	8.4	
380.....	4.0	.74	.57	8.8	
381.....	4.0	.74	.57	8.9	
382.....	4.0	.69	.57	10.0	
383.....	4.0	.64	.57	10.7	
384.....	4.0	.64	.57	10.5	
385.....	4.0	.60	.57	11.5	
386.....	4.0	.56	.57	12.9	
Temperature 1,200° C.					
Run No.	Weight of carbon, grams	Particle size mesh (U.S. standard) ¹	Inlet CO ₂ rate ¹	He rate ¹	Outlet (CO)/(CO ₂) ¹
275.....	2.00	30-40	17.9	0.77	0.190
276.....	2.00	50-60	8.8	.77	.423
277.....	3.00	50-60	8.8	.77	.54
278.....	4.00	50-60	8.8	.77	.85
279.....	6.00	50-60	8.8	.78	1.08
280.....	1.40	80-100	2.51	.226	1.15
281.....	1.75	80-100	2.51	.224	1.55
282.....	2.10	80-100	2.51	.220	2.03
283.....	2.45	80-100	2.51	.224	2.36
284.....	2.80	80-100	2.51	.224	2.85
285.....	3.15	80-100	2.51	.224	3.62
286.....	3.50	80-100	2.51	.224	4.43
287.....	4.20	80-100	2.51	.224	6.0
288.....	4.90	80-100	2.51	.224	6.6
289.....	2.80	80-100	1.25	.381	5.2
290.....	3.15	80-100	1.25	.381	5.2
291.....	3.50	80-100	1.25	.379	6.5
292.....	4.20	80-100	1.25	.379	6.5
293.....	4.90	80-100	1.25	.379	9.9
294.....	5.60	80-100	1.25	.379	17.3
295.....	2.00	30-40	17.7	.077	.213

¹ Cm.³/sec., STP (standard temperature and pressure).

TABLE 2.—Influence of inert gas on the reaction of carbon dioxide with a high-temperature metallurgical coke.¹

Run No.	N ₂ rate ²	(CO)/(CO ₂) ²	Inlet partial press., CO ₂	f ³
249	0.000	1.33	1.00	0.40
250	.157	1.22	.89	.38
251	.336	1.31	.79	.40
252	.61	1.28	.68	.39
253	.92	1.30	.58	.39
254	1.41	1.20	.48	.38
255	2.11	1.12	.38	.36
256	3.07	1.10	.30	.36

Run No.	He rate ²	(CO)/(CO ₂) ²	Inlet partial press., CO ₂	f ³
257	0.000	1.22	1.00	0.38
258	.112	1.39	.92	.41
259	.300	1.26	.81	.39
260	.58	1.38	.69	.41
262	1.24	1.29	.51	.39
263	1.92	1.27	.40	.39
264	2.82	1.17	.31	.37

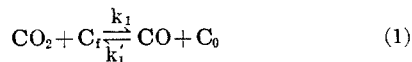
¹ Temperature 1,090° C., weight of coke 3 g., particle size 100–140 mesh (U.S. standard), CO₂ flow rate 1.28 cm.³/sec. (STP).

² cm.³/sec. (STP).

³ Fraction CO₂ reacted (by oxygen balance).

Theoretical Development

The reduction of carbon dioxide to carbon monoxide on the surface of carbon and the reverse reaction may be expressed as



where C_f represents a free site capable of reaction and C_0 a site possessing an oxygen atom. Gasification, that is, the transfer of carbon from solid phase to gas phase, originates from the occupied sites and may be expressed as



where n is an integer having a value of 0, 1, or 2, when occupied sites are considered individually. Statistically n can have any value between 0 and 2. If $n > 1$, the number of reaction sites will increase with gasification; hence, the solid will become more active with burn off. If $n = 1$, reaction rate will remain constant during an experiment involving no loss of weight of solid or a negligible loss; that is, a steady state can be maintained. If $n < 1$, the solid will become less active with gasification. In the following derivation the case $n = 1$ will be considered.

The instantaneous rate of gasification of a carbon sample surrounded by a gas having a uniform composition may be expressed as

$$dn/dt = N_C = k_3(C_0)W \quad (3)$$

where N_C is the rate of carbon transfer, atoms per second, (C_0) is the number or concentra-

tion of occupied sites per gram, and W is the weight of carbon in grams. In flow experiments gas composition is not uniform, and equation (3) would have to be restricted to a differential amount of solid

$$dN_C = k_3(C_0)dW. \quad (4)$$

Under steady-state conditions the rate of formation of occupied sites would be equal to the rate of their disappearance

$$d(C_0)/dt = k_1(\text{CO}_2)(C_f) - k'_1(\text{CO})(C_0) = 0 \quad (5)$$

where (CO_2) and (CO) represent the concentrations of CO₂ and CO in the gas phase. Expressing the total number of reaction sites by (C_t)

$$(C_t) = (C_0) + (C_f) \quad (6)$$

and solving equation (5) for (C_0)

$$(C_0) = \frac{k_1(\text{CO}_2)(C_t)}{k_1(\text{CO}_2) + k'_1(\text{CO}) + k_3} \quad (7)$$

The occurrence of oxygen exchange reactions at temperatures approximately 200° C. lower than gasification at comparable rates suggests that $k_1(\text{CO}_2) > k_3$ and/or $k'_1(\text{CO}) > k_3$. Hence k_3 may be neglected in the denominator of equation (7)

$$(C_0) = \frac{C_t}{1 + (\text{CO})/K_1(\text{CO}_2)} \quad (8)$$

where

$$K_1 = k_1/k'_1. \quad (9)$$

Omission of k_3 in the denominator of equation (7) is a simplifying assumption, and it would not be permissible for experiments under vacuum. Substitution of equation (8) into (4) and rearrangement lead to

$$[K_1 + (\text{CO})/(\text{CO}_2)]dN_C = K_1k_3(C_t)dW. \quad (10)$$

For isothermal fluidized beds when no CO is admitted at the inlet, oxygen and carbon balances between the inlet and the differential section yield

$$N_C = N_{\text{CO}_2}^{\circ} - N_{\text{CO}_2} = N_{\text{CO}}/2 \quad (11)$$

where N_{CO_2} and N_{CO} denote the flow rates of the gases designated and the superscript \circ denotes the condition at the inlet. Substituting equation (11), and

$$X = N_{\text{CO}}/N_{\text{CO}_2}^{\circ} = 2N_{\text{CO}_2}/N_{\text{CO}_2}^{\circ} - 2 \quad (12)$$

into equation (10), and integrating equation (10) for the case of negligible backmixing lead to

$$2(1 + 2/X) \ln(1 + X/2) - 2 = -K_1 + K_1k_3(C_t)(1 + 2/X)W/N_{\text{CO}_2}^{\circ}. \quad (13)$$

At low flow rates diffusion can mix the gases completely; that is, the composition gradient along the length of the column can disappear. Under these conditions N_{CO}/N_{CO_2} would be the same throughout the bed. Integration of equation (10) then yields

$$X = -K_1 + K_1 k_3 (C_t) (1 + 2/X) W / N_{CO_2}^0 \quad (14)$$

In integrating the right side of equation (10) it is tacitly assumed that composition of the gas phase inside a particle is uniform and identical to that surrounding the particle.

When CO is admitted at the inlet equations (13) and (14) take the forms

$$\frac{(2+X)(2+X^0)}{X-X^0} \ln \frac{2+X}{2+X^0} - 2 = -K_1 + K_1 k_3 (C_t) (2+X) W / (X-X^0) N_{CO_2}^0 \quad (15)$$

and

$$X = -K_1 + K_1 k_3 (C_t) (2+X) W / (X-X^0) N_{CO_2}^0 \quad (16)$$

respectively.

As stated earlier it is permissible to assume $n=1$ if there is little or no burn-off effect during a run. Changes in the gas-phase composition were not noticeable during the completion of a

run, but if the reaction were continued, up to 30 percent burn off, changes in the gas-phase composition could be accounted for by the weight loss of the coke. If the gas phase had an influence on the concentration of reaction sites, a phenomenon revealed by the hysteresis effect when gas-phase composition is changed, mixing of the granular coke particles in the fluidized state would tend to minimize this effect. Changes in the concentration of reaction sites with temperature, pressure, or excessive burn off would not affect the above equations, as they are derived for isothermal conditions, integration being performed only with respect to the length of the fluidized column, that is, not with respect to temperature or time.

Application of Theory and Discussion of Results

DETERMINATION OF THE OXYGEN EQUILIBRIUM AND THE RATE CONSTANTS

The fraction of carbon dioxide reacted is presented in figure 3 as a function of the ratio of the

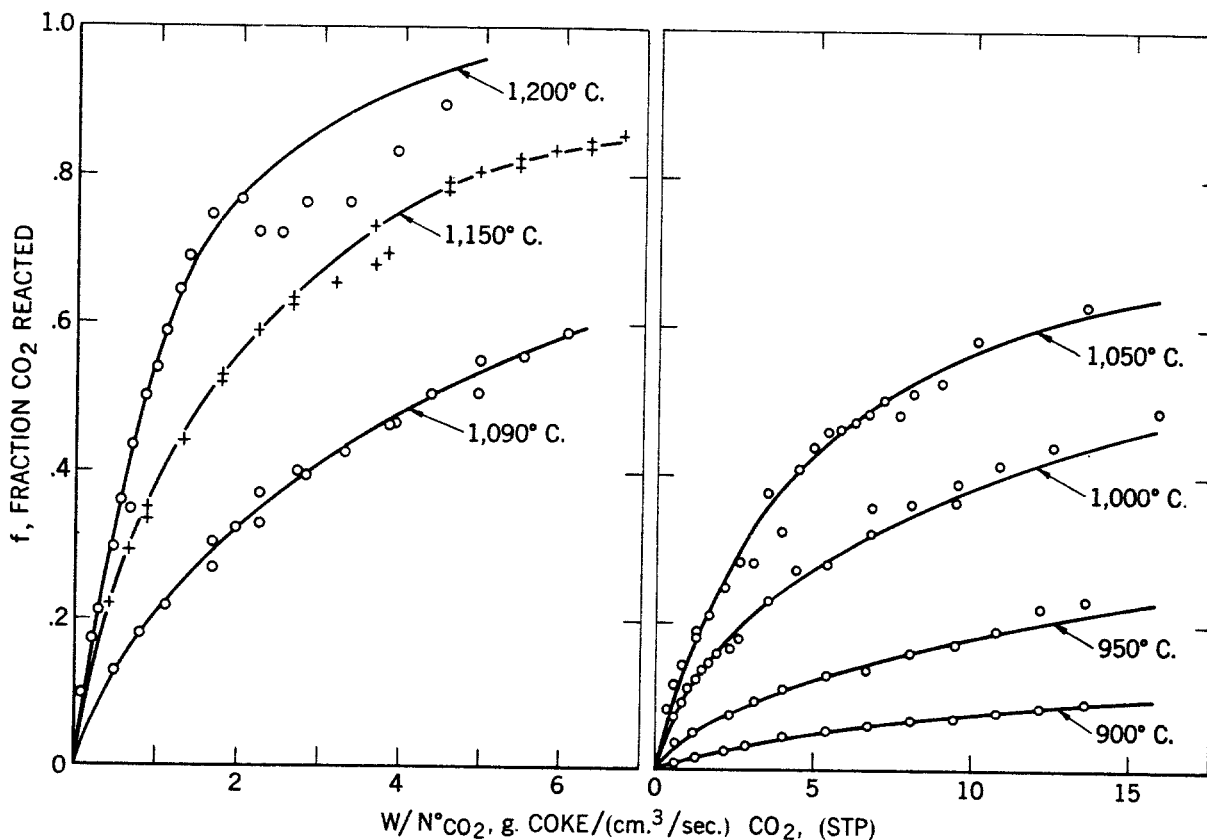


FIGURE 3.—Reaction of Carbon Dioxide With a Metallurgical Coke.

amount of coke sample to the inlet carbon dioxide flow rate. At low temperatures the reaction rate is slow, and, in order to obtain accurately measurable conversion, it is necessary to employ low flow rates. At low flow rates diffusion in the gas phase can mix the gases almost completely; that is, the composition gradient along the length of the bed can disappear. Under these conditions equation (14) should be applicable, and graphical representation of the data by the equation should yield a straight line. In figure 4 data obtained at 900° C. are shown as an illustration of this case. Such a plot yields the values of the equilibrium and rate constants, the intercept on the abscissa corresponding to the value of $1/k_3(C_t)$ and the negative intercept on the ordinate to the value of K_1 . At high temperatures, on the other hand, reaction rate is fast, and in order to prevent nearly complete conversion, a measure necessary for kinetic analysis, high gas velocities are employed. Under these conditions back mixing by diffusion becomes negligible, and equation (13) should be applicable. Data obtained at 1,200° C. illustrate this case in figure 4.

Comparison of equations (13) and (14) shows that their right sides are identical. Because their left sides are not linear with each other over wide ranges of values of X , except as X approaches zero, experimental data that yield a straight line on one type of plot do not yield a straight line on the other. In case of partial mixing, both plots may yield curves. However, extrapolation of the lines to the point where they cross the abscissa is identical with the determination of the instantaneous rate at the inlet where the conversion is zero; when $(CO)/(CO_2)=0$, equation (10) reduces to $dW/dN_c=1/k_3(C_t)$ under all conditions of flow. Hence both plots cross the abscissa at the same value as illustrated in the middle plot of figure 4. On the other hand, plots obtained by equations (13) and (14) lead to K_1 values that differ by a factor of 2. This factor can also be predicted analytically, for when X approaches zero, the left side of equation (14) becomes identical with $X/2$ as compared with X of equation (13).

Whenever it becomes difficult to ascertain which flow condition prevailed, an average value of K_1 as determined from both plots can be used. However, for better results a graphical integration of equation (10) should be performed. This can be accomplished from plots of $(CO)/(CO_2)$ as a function of $N_c/N^\circ CO_2$ and W/N_c as a function of $N_c/N^\circ CO_2$. From the two plots one obtains the values of $(1/N_c) \int (CO)/(CO_2) dN_c$ and W/N_c , and their graphical representations yield the values of K_1 and $k_3(C_t)$. The procedure has been used in determining the constants reported in this paper. The graphical integra-

tion will be illustrated for the more complicated steam-coke reactions.

Once the values of K_1 and $k_3(C_t)$ are obtained, it becomes possible to construct conversion curves as a function of the ratio of amount of coke to inlet flow rate of carbon dioxide by graphical methods or by the use of equation (13) or (14) or both, depending upon the prevailing flow conditions. The close match between the calculated curves (solid lines in figure 3) and experimental data indicates that flow conditions have been properly predicted or proper values of K_1 and $k_3(C_t)$ have been determined.

INFLUENCE OF PARTICLE SIZE

One of the first factors studied was particle size. For porous carbons³⁰ the reaction rate was found to be independent of particle size in the size range of 0.08 to 1.8 mm. However, this finding may not extend to particle sizes outside this range. The particle sizes used in the data presented here were dictated by flow rates required for fluidization and for purposes of covering wide ranges of carbon dioxide conversion.

INFLUENCE OF INERT GAS

To determine the influence of inert gas, helium or nitrogen was introduced at successively increased rates while the flow rate of carbon dioxide and amount of the coke remained the same (table 2). As seen in figure 5, helium and nitrogen had no effect on the reaction rate as expected from the present theory. The fact, that the reaction rate is independent of the concentration of inert gas but dependent upon the $(CO_2)/(CO)$ ratio in the gas phase clearly illustrates the impropriety of the use of partial pressure indiscriminately in the kinetic analysis of heterogeneous reactions. The same conclusion could be reached if one considers that partial pressure can be varied by changing either the flow rate of the reactant gas or of inert gas or by introducing product gases; hence, partial pressure cannot be treated as an independent variable in kinetic functions.

INFLUENCE OF SPACE VELOCITY

An increase in the flow rate of inert gas while keeping the flow rate of carbon dioxide constant increases the velocity of gas flow in the column, that is, space velocity. From the previously mentioned experiments one might conclude that space velocity has no influence on the reaction

³⁰ Ergun, S., Kinetics of the Reaction of Carbon Dioxide with Carbon: Jour. Phys. Chem., vol. 60, 1956, pp. 480-485.

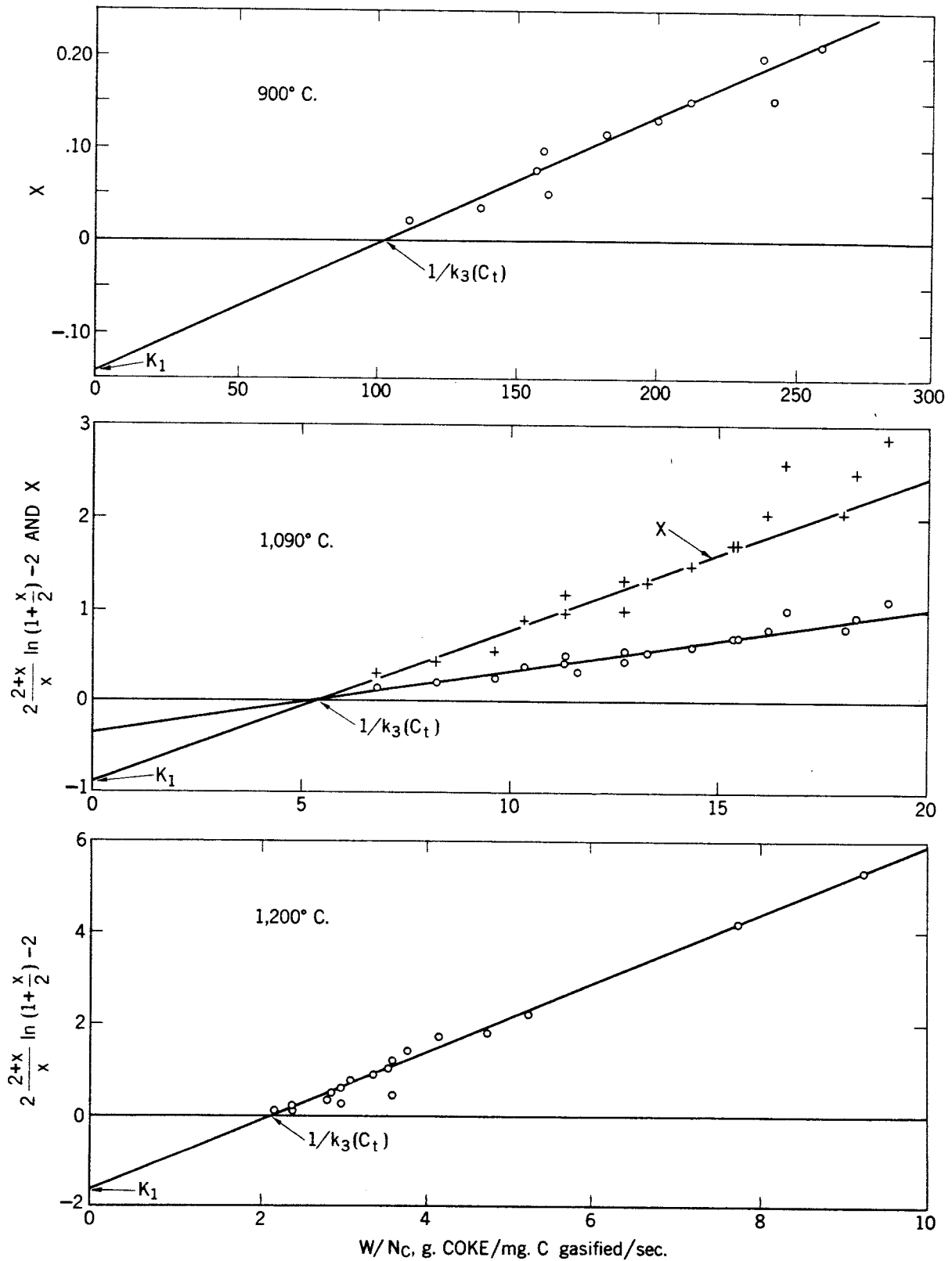


FIGURE 4.—Determination of the Parameters of the Reactions of Carbon Dioxide With a Metallurgical Coke.

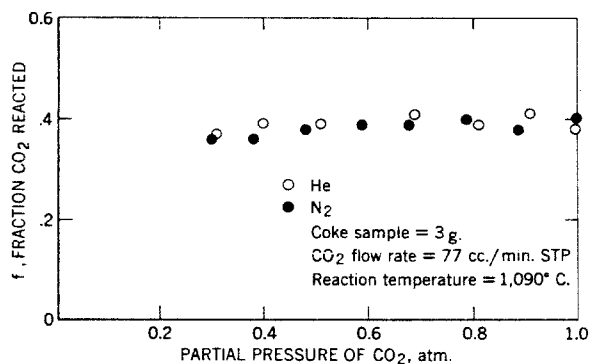


FIGURE 5.—Effect of Inlet Partial Pressure of Carbon Dioxide on Fraction of Carbon Dioxide Decomposed at Constant Flow Rate of Carbon Dioxide.

rate. However, this conclusion would not be true if increase in space velocity were achieved by increasing the flow rate of carbon dioxide while keeping the amount of coke constant (see runs 322-6 and 327-36, table 1, p. 12). Since increase in space velocity can be achieved by changing the flow rate of inert gas or reactant gas, space velocity cannot be used as an independent variable in kinetic analysis.

From equations (13) and (14) it follows that X , hence fraction of CO_2 reacted $f = X/2 + X$, is a function of the ratio of the weight of the coke to the inlet flow rate of CO_2 . This is demonstrated in figure 3 where the solid lines are calculated by the use of equations (13) or (14). It is seen that at any temperature a single curve can be constructed expressing the fraction of carbon dioxide reacted as a function of $W/N^\circ_{\text{CO}_2}$. However, it is not possible to construct a single curve for the gasification rate N_c . The experiments performed for investigating the role of inert gas concentration and space velocity clearly showed that gas-phase (film-boundary) diffusion had no influence on the reaction rate; that is, diffusion was too rapid to have any influence.

COMPARISON OF COKE DATA WITH DATA OF RELATIVELY PURE CARBONS

The experimentally determined values of equilibrium constant K_1 of the oxygen exchange reaction are plotted as a function of temperature in figure 6. Dashed lines obtained with relatively pure carbons³¹ are also included in the figure. It is seen that coke data are of the same order of magnitude. At low temperatures, values of K_1 for coke are lower; at 1,200° C., they become identical with those of relatively pure carbons. The apparent heat of reaction is about 27 kcal./mole for coke as compared

with 23 kcal./mole for carbons. These differences, however, are not insignificant from a fundamental point of view. The differences could be explained by the mineral matter present in coke. Iron compounds and other mineral matter are known to react with carbon dioxide and carbon monoxide; they may be involved in oxygen exchange reactions and influence the oxygen concentration in the solid carbon. Such an influence, if present, apparently diminishes above 1,150° C.

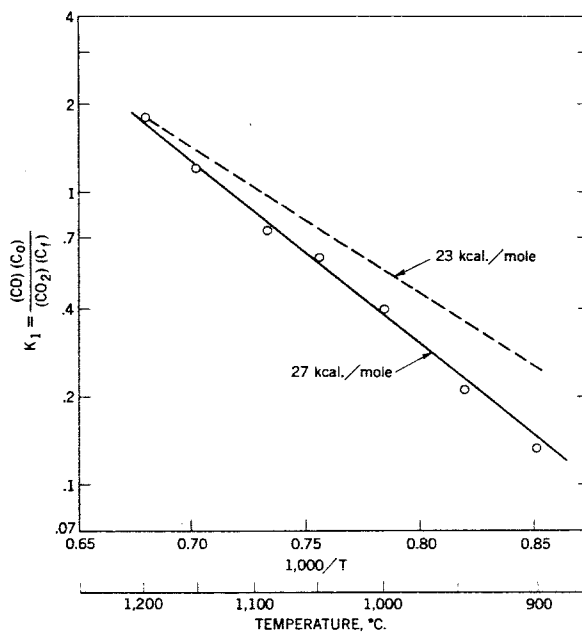


FIGURE 6.—Equilibrium Constant of the Oxygen Exchange Reaction Over Coke Between Carbon Dioxide and Carbon Monoxide as a Function of Temperature.

Another explanation concerns the solid state of carbon in coke: X-ray scattering intensities of coke change with heat treatment or with oxidation. Such changes, however, are descriptive and, for the case of metallurgical cokes, are too complicated to interpret because of the large amounts of mineral matter that these cokes contain. Moreover, in the case of relatively pure carbons (all of them heat-treated at 1,300° C. in helium atmosphere) crystallinity had no marked effect upon the values of K_1 .³² These observations, however, do not rule out the structural changes in the carbon skeleton with temperature as the cause of differences in the values of K_1 . Simultaneous kinetic and X-ray studies of cokes prepared relatively free from mineral matter (less than 1 pct.) may give better clues as to the nature of structural changes taking place with temperature.

³¹ Work cited in footnote 30, p. 15.

³² Work cited in footnote 30, p. 15.

The experimentally determined values of $k_3(C_t)$ for coke are shown in figure 7 as a function of temperature in an Arrhenius plot with data for relatively pure carbons. It is seen that at low temperatures metallurgical coke data agree closely with those of activated coke. The latter was a commercial product later demineralized with HCl-HF treatment and heat-treated at 1,300° C. in helium before kinetic experiments were conducted. At about 1,200° C., values of $k_3(C_t)$ and K_1 (fig. 6) were approximately the same as those of Ceylon graphite; that is, the metallurgical coke and the Ceylon graphite used had identical reactivities. The identity is probably a coincidence because there appears to be no other property of a metallurgical coke heated to 1,200° C. identical with that of Ceylon graphite. Moreover, the values of $k_3(C_t)$ of the Ceylon graphite depended upon particle size, and those shown in figure 7 were obtained with 80–100 mesh.³³

The change of the slope of the plot of $k_3(C_t)$ against reciprocal temperature strongly suggests that concentration of reaction sites (C_t) of cokes diminishes with temperature. A gradual decrease in the activation energy of the carbon-oxygen complex appears to be less likely because such a decrease would result in an increase in the heat of reaction of the oxygen exchange reaction at high temperatures. As seen in figure 6, an opposite effect, if any, is detected. A decrease in the concentration of reaction sites is in accordance with the postulations of Strickland-Constable³⁴ and Duval.³⁵

³³ Work cited in footnote 30, p. 15.

Changes in the solid state of coke with temperature will be discussed further when steam-coke reactions are considered.

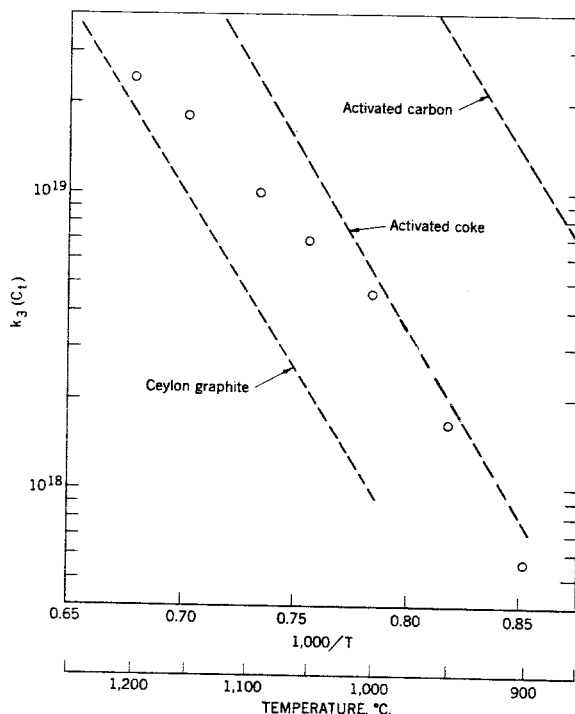


FIGURE 7.—The Constants of the Gasification Step as a Function of Temperature.

³⁴ Strickland-Constable, R. F., Interaction of Carbon Filaments at High Temperatures with Nitrous Oxide, Carbon Dioxide, and Water Vapor: *Trans. Faraday Soc.*, vol. 43, 1947, pp. 769–778.

³⁵ Duval, X. [Kinetics of the Combustion of Carbon at High Temperatures and Low Pressures]: *Ann. Chim.*, vol. 10, 1955, pp. 903–967.