

equilibrium under certain conditions, is that some sort of diffusional hindering of the reaction is involved that is not manifested by particle size. For a better investigation of diffusional effects, experiments were conducted using steam-carbon dioxide, steam-hydrogen, and steam-carbon monoxide mixtures.

REACTIONS OF CARBON DIOXIDE-STEAM MIXTURES

For the simultaneous introduction of carbon dioxide and steam, equation (34) takes the form

$$N_{H_2} = N_{CO} + 2N_{CO_2} - 2N_{CO_2}^0 \quad (43)$$

where $N_{CO_2}^0$ is the inlet flow rate of carbon dioxide.

Similarly equation (35) takes the form

$$N_C = N_{CO} + N_{CO_2} - N_{CO_2}^0 \quad (44)$$

or

$$N_C = \frac{(K+Y)Y}{(2K+Y)(1+Y)} N_{H_2O}^0 + \frac{Y}{2K+Y} N_{CO_2}^0 \quad (45)$$

Substitution of equation (45) into (37) and integration leads to

$$u = Y - (N_{H_2O}^0/N_C) \left\{ Y + \frac{2K^2}{1-2K} \ln \frac{2K+Y}{2K} - \frac{1-K}{1-2K} \ln(1+Y) \right\} - (N_{CO_2}^0/N_C) \left(Y + 2K \ln \frac{2K+Y}{2K} \right) \quad (46)$$

By the use of equations (46) and (36), values of $W/N_{H_2O}^0$ can be calculated as a function of f for different values of $q = N_{CO_2}^0/N_{H_2O}^0$, and a series of plots of f against $W/N_{H_2O}^0$ can be constructed. Results of such calculations are shown in figure 18 for the reaction at 1,100° C. In these calculations, the values of K_2 and $k_3(C_t)$ for 1,100° C were used as determined from the plot shown in figure 11. From figure 18, it is seen that the fraction of water reacted should be decreased by the addition of carbon dioxide because of competition of carbon dioxide. For verification of this competition, special experiments were conducted employing constant amounts of coke and constant rates of flow of steam while successively increasing rate of carbon dioxide flow. The experimental results are shown in table 5 and represented graphically in figure 19. The solid line in the figure was drawn through the points taken from figure 18. It is seen that the agreement between calculations and experiments is good.

Whereas carbon dioxide suppresses the conversion of steam by competition, addition of

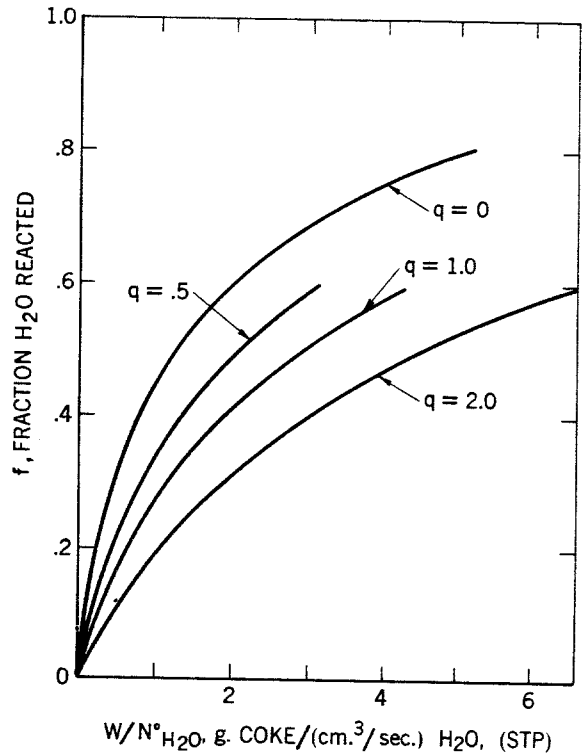


FIGURE 18.—Effect of Carbon Dioxide on Reaction of Steam With Coke.

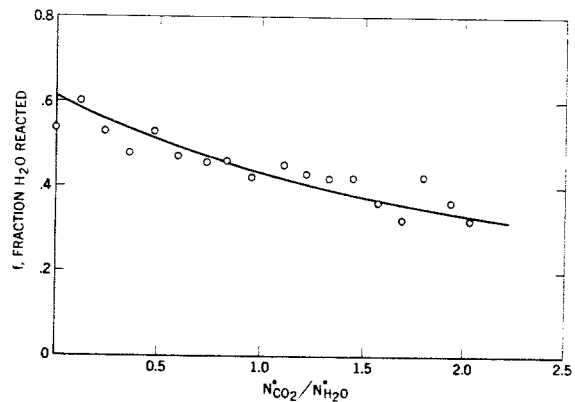


FIGURE 19.—Decrease in Steam Conversion With Addition of Carbon Dioxide.

carbon dioxide, while keeping steam flow rate constant, should increase total gasification. The increase in gasification can be calculated by using equations (36), (45), and (46). Results of such calculations are shown in figure 20. Experimentally determined values of gasification rates divided by steam flow rate are plotted in figure 21 against the carbon dioxide-steam ratio at the inlet. Calculated values as taken from the curves in figure 20 are also shown in

TABLE 5.—Reaction of steam-carbon dioxide mixtures with a high-temperature metallurgical coke at 1,100° C.¹

Run No.	CO ₂ rate ²	N ₂ rate ²	Outlet gas composition relative to N ₂ , water-free basis.			f ³	N _C /N ^o H ₂ O ⁴	$\frac{(H_2)(CO_2)}{(H_2O)(CO)}$
			CO ₂	CO	H ₂			
170	0.000	0.91	0.253	0.897	1.331	0.54	0.46	0.33
171	.267	.89	.416	1.261	1.515	.60	.55	.49
172	.533	.90	.527	1.332	1.317	.53	.51	.45
173	.806	.90	.686	1.452	1.198	.48	.50	.44
174	1.07	.90	.928	1.718	1.317	.53	.59	.61
175	1.33	.89	1.011	1.749	1.187	.47	.63	.51
176	1.60	.89	1.420	1.847	1.150	.46	.59	.65
177	1.87	.90	1.539	2.097	1.152	.46	.63	.63
178	2.13	.90	1.758	2.047	1.050	.42	.59	.62
179	2.50	.94	2.004	2.204	1.062	.45	.66	.74
180	2.72	.93	2.188	2.291	1.031	.43	.63	.72
181	2.97	.91	2.368	2.522	1.040	.42	.67	.68
182	3.24	.91	2.637	2.642	1.036	.42	.69	.72
183	3.53	.91	2.581	2.552	.885	.36	.71	.57
184	3.79	.91	2.647	2.485	.784	.32	.70	.50
185	4.03	.91	3.308	3.178	1.025	.42	.83	.75
186	4.35	.91	3.510	3.017	.898	.36	.71	.67
187	4.56	.91	3.479	2.816	.796	.32	.72	.58

¹ Weight of sample 5 g., H₂O rate 2.24 cm.³/sec. (STP).

² cm.³/sec. (STP).

³ Fraction H₂O reacted (by hydrogen balance).

⁴ g. atom C/g. mole H₂O.

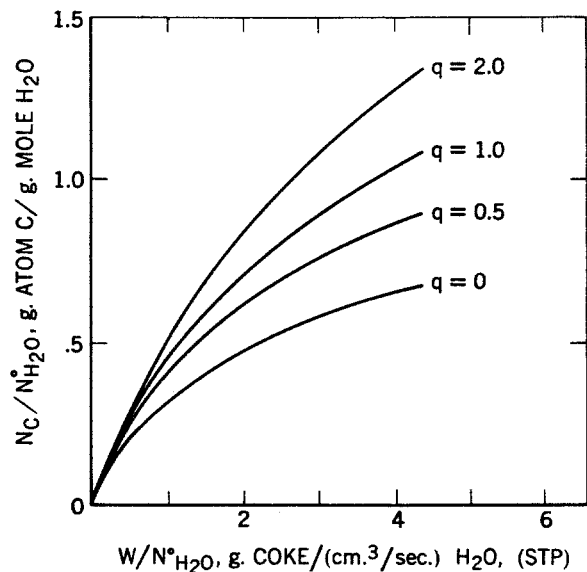


FIGURE 20.—Effect of Carbon Dioxide Addition on Total Gasification of Coke.

figure 21 as a solid line. It is seen that the experimental values are lower than those calculated. The difference is easily explained by the fact that the value of $k_3(C_t)$ used in the calculations of the solid line was determined from steam reactions. If composite values of $k_3(C_t)$ proportional to the mole fractions of

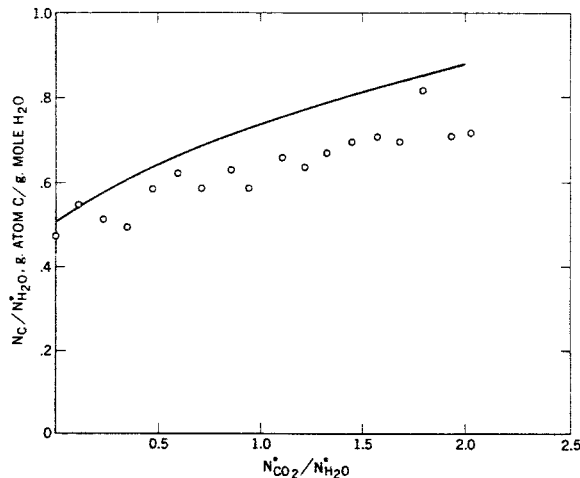


FIGURE 21.—Increase in Total Gasification With Addition of Carbon Dioxide.

steam and carbon dioxide are used, the dashed line shown in figure 21 is calculated. The agreement between the calculations and the experiments is good.

From these results it is seen that the gasification rates of coke with steam-carbon dioxide mixtures can be predicted by the use of the rate constants obtained from separate experiments. If the reactions of these gases involve their diffusion through pores into the interior

of the particles, such diffusion must be very fast in order not to influence the overall reaction rates. Otherwise, differences in the diffusion coefficients of these two gases would certainly influence the rates of their simultaneous reactions. An alternate explanation is that the chemisorbed oxygen is mobile, that is, possesses one or two degrees of translational energy, and that the penetration of carbon dioxide and/or steam into the interiors of solid plays a minor role. The rate of oxygen migration would not be affected by the gas phase in the pore system.

Outlet gas compositions are plotted in figure 22 for the purposes of observing if water-gas shift equilibrium is maintained in the gas phase. It is seen that an overshift is attained. Slight errors in gas analysis are exaggerated in this type of plot; however, systematic high values are difficult to explain. The explanation of this effect is probably tied with the differences in the $k_3(C_t)$ values of steam and carbon dioxide.

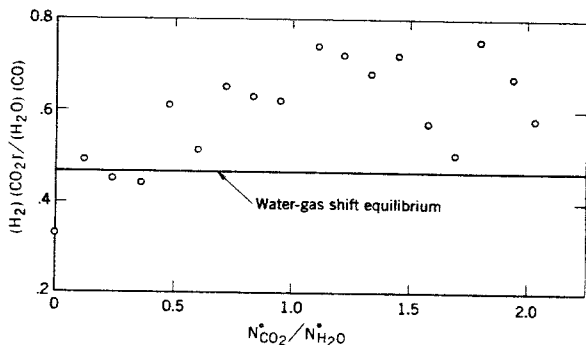


FIGURE 22.—Outlet Gas Composition as a Function of Carbon Dioxide-to-Steam Ratio at Inlet.

REACTIONS OF HYDROGEN-STEAM MIXTURES

For the case of simultaneous introduction of steam and hydrogen equations (32) and (35) take the forms

$$N_{H_2} = Y(1 + Y^{\circ})N_{H_2O}^{\circ} / (1 + Y) \quad (47)$$

and

$$N_C / N_{H_2O}^{\circ} = (K + Y)(Y - Y^{\circ}) / (2K + Y)(1 + Y), \quad (48)$$

respectively. In the above equations, Y° is the ratio of hydrogen to steam at the inlet. Substituting equation (48) into (36) and integrating

$$\frac{(1-K)(1+Y^{\circ})}{1-2K} \ln \frac{1+Y}{1+Y^{\circ}} - \frac{K(2K+Y^{\circ})}{1-2K} \ln \frac{2K+Y}{2K+Y^{\circ}} - (Y+Y^{\circ}) \left\{ 1 - \frac{(K+Y)(K_2+Y)}{(2K+Y)(1+Y)} \right\} = K_2 k_3(C_t) W / N_{H_2O}^{\circ} \quad (49)$$

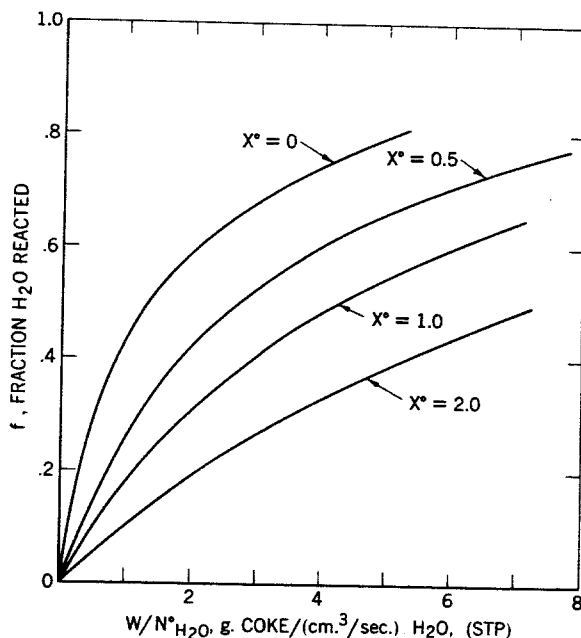


FIGURE 23.—Effect of Hydrogen on Reaction of Steam With Coke.

Equation (49) can also be expressed in terms of fraction of steam reacted by substituting $Y = (f + Y^{\circ}) / (1 - f)$.

From a knowledge of K_2 and $k_3(C_t)$ a series of f against $W / N_{H_2O}^{\circ}$ curves can be constructed for different values of Y° by the use of equation (49). Results of such calculations are shown in figure 23 for the steam-coke reaction at $1,100^{\circ} C$. From the figure the retardation effects of hydrogen on the conversion of steam can be calculated. To verify this effect exper-

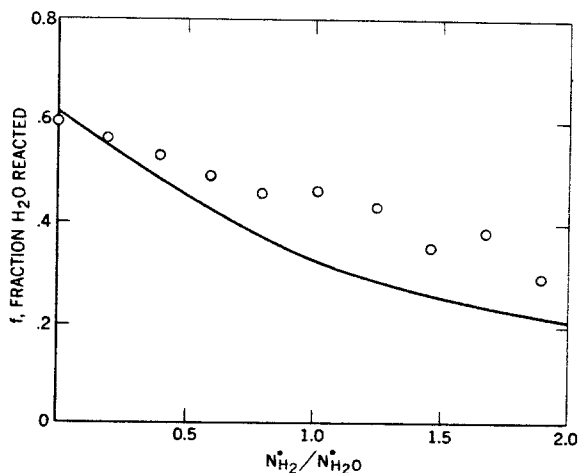


FIGURE 24.—Decrease in Steam Conversion With Addition of Hydrogen.

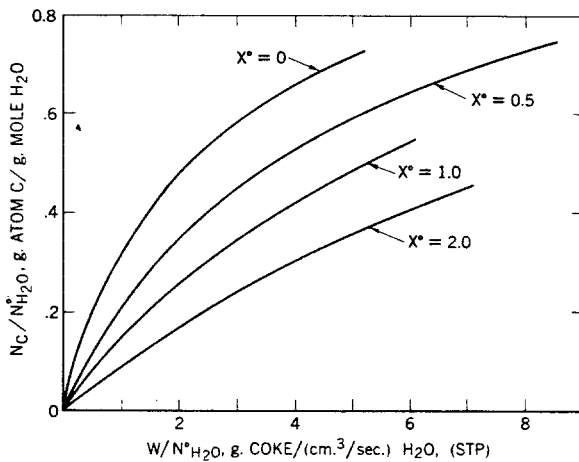


FIGURE 25.—Effect of Hydrogen on Gasification of Coke With Steam.

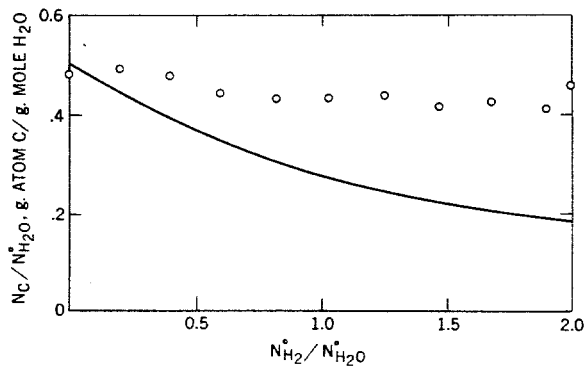


FIGURE 26.—Decrease in Gasification With Addition of Hydrogen.

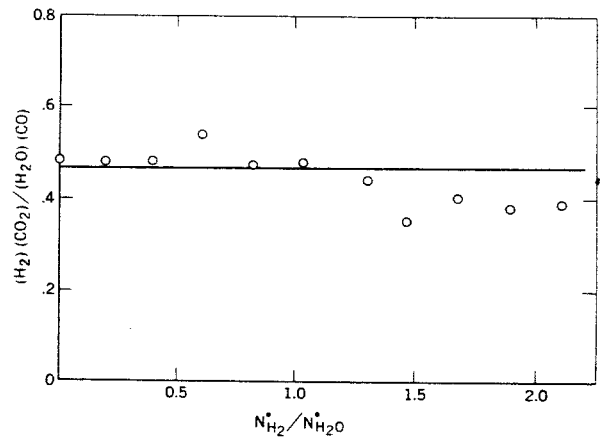


FIGURE 27.—Outlet Gas Composition as a Function of Hydrogen-to-Steam Ratio at Inlet.

iments were conducted at constant steam flow rates while the rate of hydrogen flow was successively increased. The results are listed in table 6. The experimental and calculated results are shown in figure 24. It is seen that there is a retardation effect but not as much as expected.

The retardation effect of hydrogen on the gasification rate can also be calculated by the use of equations (48) and (49) as shown in figure 25. The calculated and the experimental results (see table 6) are represented graphically in figure 26. It is seen that the retardation effects were much less than calculated. To show the effects of hydrogen on the water-gas shift equilibrium, the outlet gas compositions are represented graphically in figure 27 as a

TABLE 6.—Reaction of steam-hydrogen mixtures with a high-temperature metallurgical coke at 1,100° C.¹

Run No.	H ₂ rate ²	N ₂ rate ²	Outlet gas composition relative to N ₂ , water-free basis.			f ³	N _C /N _{H₂O} ⁴	$\frac{(H_2)(CO_2)}{(H_2O)(CO)}$
			CO ₂	CO	H ₂			
200	0.00	0.90	0.302	0.904	1.473	0.59	0.48	0.48
201	.441	.90	.267	.967	1.895	.56	.50	.48
202	.894	.90	.232	.956	2.312	.53	.48	.48
203	1.35	.90	.201	.903	2.732	.49	.44	.54
204	1.83	.90	.182	.903	3.181	.46	.44	.47
205	2.30	.90	.159	.916	3.692	.46	.43	.48
206	2.80	.90	.143	.945	4.171	.43	.44	.44
207	3.27	.91	.115	.908	4.467	.35	.42	.35
208	3.77	.91	.117	.953	5.088	.38	.43	.40
209	4.26	.90	.112	.911	5.479	.30	.41	.38
210	4.72	.90	.086	1.037	6.344	.45	.46	.39

¹ Weight of sample 5 g., H₂O flow rate 2.24 cm.³/sec. (STP).

² cm.³/sec. (STP).

³ Fraction H₂O reacted (by hydrogen balance).

⁴ g. atom C/g. mole H₂O.

function of hydrogen-to-steam ratio at the inlet, and as seen from the figure, water-gas shift equilibrium was more or less maintained.

These results suggest that an inward diffusion of gases through the pore system of the solids may not be involved and that hydrogen escaped, that is, flowed upward in the gas stream. Otherwise, a highly diffusing gas like hydrogen would have effectively reduced the concentration of oxidized reaction sites. This observation implies that there are differences in the composition of gas in the stream and the gas in the pores and hence a concentration gradient of oxygen in the solid phase.

REACTIONS OF CARBON MONOXIDE-STEAM MIXTURES

When carbon monoxide and steam are introduced simultaneously, equations (34), (35), and (39) are modified to take the forms

$$N_{H_2} = N_{CO} - N_{CO}^0 + 2N_{CO_2} \quad (50)$$

$$N_C/N_{H_2O}^0 = (K+Y)Y/(2K+Y)(1+Y) - Kr/(2K+Y) \quad (51)$$

and

$$u = Y - (N_{H_2O}^0/N_C)(Y - Y^0) + \frac{2K^2}{1-2K} \ln \frac{2K+Y}{2K+Y^0} - \frac{1-K}{1-2K} \ln \frac{1+Y}{1+Y^0} + (N_{CO}^0/N_C)K \ln \frac{2K+Y}{2K+Y^0} \quad (52)$$

respectively. In the above equation Y^0 denotes the initial water-gas reaction and is obtained by

$$(K+Y^0)Y^0/(1+Y^0) = Kr \quad (53)$$

where r is the inlet ratio of carbon monoxide to steam, that is, $r = N_{CO}^0/N_{H_2O}^0$. Substitution of equation (52) into (36) and proper rearrangement lead to

$$\frac{1-K}{1-2K} \ln \frac{1+Y}{1+Y^0} - \left\{ \frac{2K^2}{1-2K} + Kr \right\} \ln \frac{2K+Y}{2K+Y^0} - \frac{K_2 Y}{2K+Y} \left\{ \frac{Y(K+Y)}{1+Y} - Kr \right\} - (Y - Y^0) = K_2 k_3 (C_s) W/N_{H_2O}^0 \quad (54)$$

By calculating the values of $W/N_{H_2O}^0$ as a function of $f = Y/(1+Y)$, one can construct a series of curves for different values of r and observe the effect of r on f . Calculations made for reactions at 1,100° C. are shown in figure 28. The equations derived for carbon monoxide-

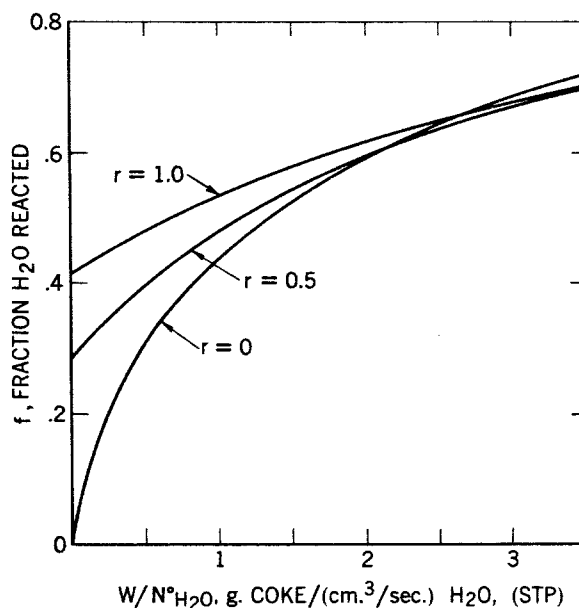


FIGURE 28.—Effect of Carbon Monoxide on Reaction of Steam With Coke.

steam mixtures are not strictly applicable because the assumption of water-gas shift equilibrium requires an initial instantaneous equilibrium which, of course, is not attained. Theoretically, one would obtain an increase in the fraction of steam decomposed when the gasification is low mainly due to water gas reaction, reverse effects being obtained when steam concentration becomes low. Experi-

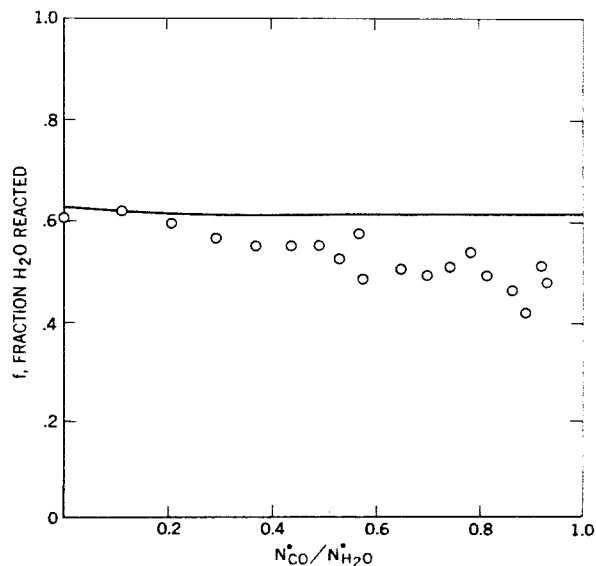


FIGURE 29.—Change in Steam Conversion With Addition of Carbon Monoxide.

TABLE 7.—Reaction of steam-carbon monoxide mixtures with a high-temperature metallurgical coke at 1,100° C.¹

Run No.	CO rate ²	N ₂ rate ²	Outlet gas composition relative to N ₂ , water-free basis.			f ³	N _C /N \dot{H}_2 O ⁴	(H ₂)(CO ₂)/(H ₂ O)(CO)
			CO ₂	CO	H ₂			
211	0.000	0.90	0.276	0.897	1.502	0.60	0.47	0.47
212	.244	.90	.348	1.042	1.476	.59	.46	.48
213	.463	.90	.369	1.195	1.471	.59	.42	.45
214	.659	.90	.458	1.216	1.408	.57	.38	.49
215	.829	.90	.487	1.310	1.368	.55	.35	.45
216	.972	.90	.507	1.432	1.366	.55	.35	.43
217	1.10	.90	.520	1.540	1.365	.55	.34	.41
218	1.19	.91	.544	1.540	1.296	.52	.30	.39
219	1.27	.91	.579	1.789	1.414	.57	.34	.43
220	1.46	.90	.574	1.702	1.243	.50	.27	.34
221	1.57	.91	.570	1.790	1.223	.50	.26	.32
222	1.66	.91	.571	1.938	1.250	.51	.28	.30
223	1.76	.91	.588	2.128	1.327	.54	.30	.32
224	1.83	.91	.560	2.106	1.214	.49	.26	.26
225	1.93	.91	.555	1.993	1.141	.46	.24	.24
226	1.99	.91	.500	1.823	1.029	.42	.22	.20
227	2.06	.91	.570	2.370	1.258	.51	.28	.25
228	2.08	.91	.589	2.433	1.183	.48	.24	.22

¹ Weight of sample 5 g., H₂O rate 2.24 cm.³/sec. (STP).

² cm.³/sec. (STP).

³ Fraction H₂O reacted (by hydrogen balance.)

⁴ g. atom C/g. mole H₂O.

ments were conducted under conditions where these curves come together, those for $W/N_{H_2O}^0 = 2.23$ g. coke/cm.³ H₂O (STP). The results are tabulated in table 7 and are shown in figure 29 with calculated results. It is seen that, in contrast to hydrogen, carbon monoxide had a retarding influence which was slightly more than that calculated. This effect can be explained by the fact that water-gas reaction was not fast enough and/or that outward motion of carbon monoxide formed inside the particles is hindered.

The retardation effect of carbon monoxide is best observed when rates of gasification are considered (fig. 30). Experimental and calculated results are plotted in figure 31. Again, in contrast to hydrogen, carbon monoxide had a slightly more retarding influence than calculated. The differences, although not excessive, may be significant. The data of table 7 are also represented graphically in figure 32 to show the influence of carbon monoxide on the water-gas shift equilibrium. It is seen that water-gas reaction was not fast enough to accommodate excessive amounts of carbon monoxide. The effects observed in figures 29, 31, and 32 are consistent with each other.

The higher retarding influence of carbon monoxide than that of hydrogen observed in this study appears to be contrary to the opposite conclusions of some investigators. For pur-

poses of comparison of carbon monoxide and hydrogen data, data shown in figures 24, 26, 29, and 31 are reproduced in figure 33. From a superficial analysis of the plot at the top of the figure, one might conclude that hydrogen has a

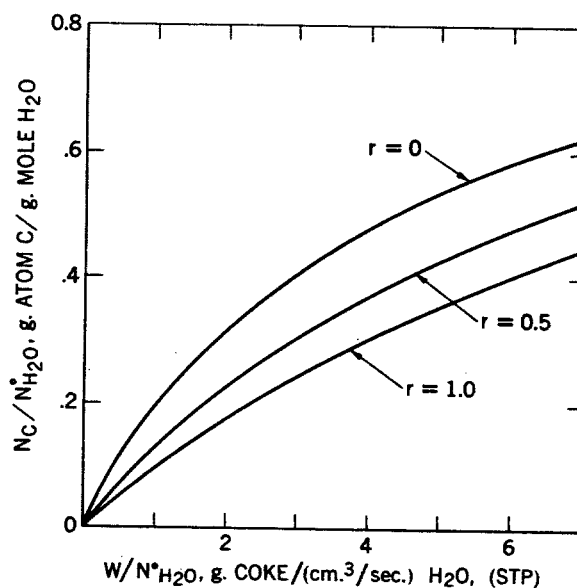


FIGURE 30.—Effect of Carbon Monoxide on Gasification of Coke With Steam.

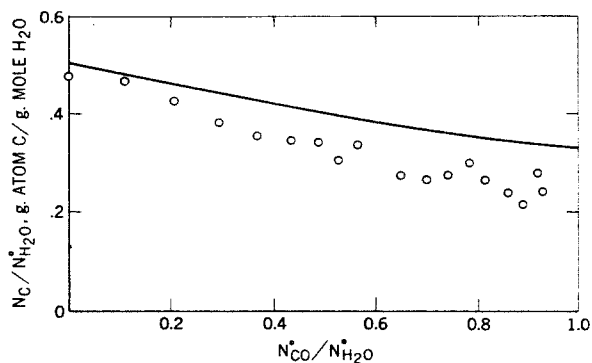


FIGURE 31.—Decrease in Gasification With Addition of Carbon Monoxide.

slightly higher or an equal retarding effect than that of carbon monoxide. If, on the other hand, the influence of these gases on the rate of gasification of coke is considered (bottom of figure 33), it is observed that carbon monoxide has a more retarding influence. From figure 33 and the preceding separate analyses of the influence of these gases it is seen that any conclusion regarding retardation would be arbitrary, if not meaningless, unless such analyses are done in the light of the influence of all of the reactions involved.

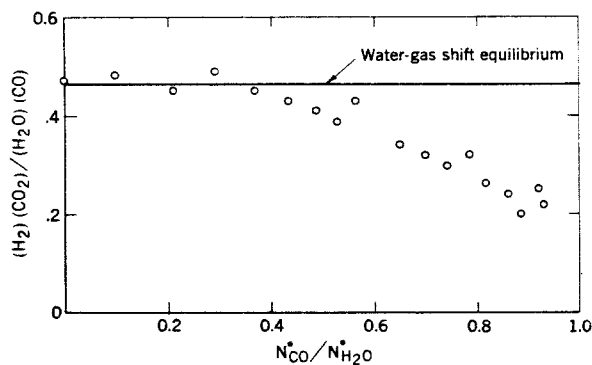


FIGURE 32.—Outlet Gas Composition as a Function of Carbon Monoxide-to-Steam Ratio at Inlet.

THE EFFECT OF MACROPOROSITY OF COKE ON GASIFICATION RATES

As shown earlier, the particle size of the granular coke used in steam and carbon dioxide reactions had no marked influence on the reaction rates. This fact suggests that diffusional processes involved in the reaction of coke have little or no influence on the rate of reaction. While this suggestion is in accordance with most of the observations made in this study,

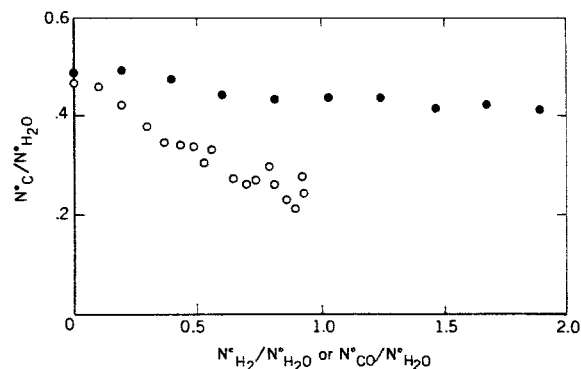
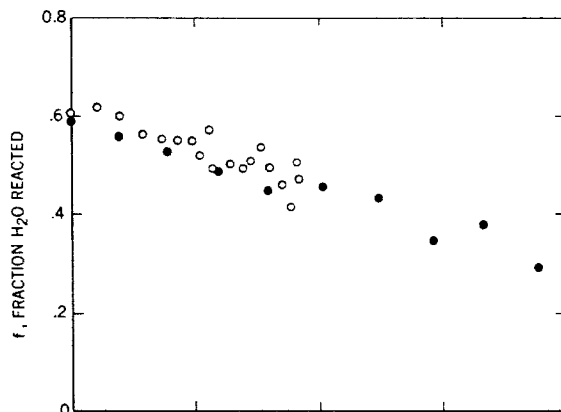


FIGURE 33.—Decrease in Steam Conversion (*Top*) and Gasification Rate (*Bottom*) With Addition of Hydrogen (+) or Carbon Monoxide (o).

for example, influence of inert gas, relation between K_1 and K_2 , reactions of carbon dioxide-steam mixtures, and reactions of hydrogen-steam mixtures, it appears to be inconsistent with some other findings, as for example, differences in the values of $k_3(C_t)$ obtained from carbon dioxide-coke and steam-coke reactions. According to the theory presented here, identical results should be obtained. If the concentration of reaction sites is influenced by the gas phase present (specifically by hydrogen) as well as by thermal energy, the differences in the values of $k_3(C_t)$ can be reconciled. While there is evidence in the literature showing excessive influence of trace amounts of hydrogen on the rate of gasification supporting this explanation, coke-carbon dioxide reactions reported here were not done in the absolute absence of hydrogen; the coke used contained some hydrogen. Moreover, in reacting simultaneously with steam, carbon dioxide behaved the same as it did when reacting alone. An alternate explanation of the difference is that there is a diffusional hindering (pore diffusion) to the escape of CO that is formed inside the particles. Since the primary product of the

reaction of CO_2 appears to be carbon monoxide and since reaction of carbon dioxide produces more carbon monoxide than the reaction of a corresponding molar amount of steam, the escape rate of carbon monoxide for the pores would be more hindered in the case of carbon dioxide reaction than in the case of steam reaction. Under such conditions the values of $k_2(C_t)$ obtained would be effective values or pseudovalues, lower values being obtained for carbon dioxide reactions. This alternate explanation is consistent with the curvature of $k_2(C_t)$ values in the Arrhenius plots (figs. 7 and 17), but it is not consistent with the steam and carbon dioxide curves being more or less parallel. The parallelism favors the former explanation. The alternate explanation also appears to be inconsistent with the lack of particle-size effect. For this reason a study of the porosity of cokes was undertaken.³⁶ Specific particle volumes of cokes depend upon particle size. This dependence is due to destruction of macropores as the size of the particle is reduced. The change in specific volume with size is therefore related to pore-size distribution. The specific volume of the coke used in this study is represented graphically in figure 34 as a function of particle size. It is seen that the specific volume is decreased from 1.08 (density=0.923 g./cc.) to 0.628 (density=1.59 g./cc.) upon reduction of size from 8-16 to 100-140 mesh. An analysis of the curve revealed that macro-

pores (120 and 420 microns in diameter) constituted about 78 percent of the total pore volume of the 8-16 mesh coke. Since the particle sizes employed in the present study were 8-16 to 140-200 mesh, *macropores may have diminished any effect that particle size may have had.* From the present study, therefore, it cannot be said that particle size would have no effect if the size ranged below 100 microns or above 2mm.

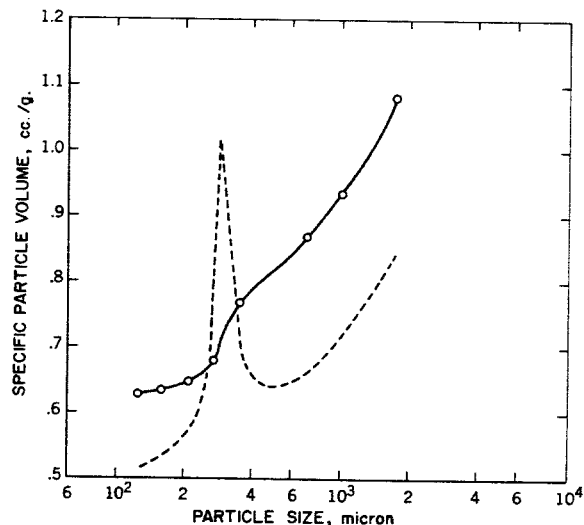


FIGURE 34.—Graphical Determination of Pore Size Distribution. Dotted line is plot of slope of solid line leading to pore size distribution.

³⁶ Ergun, S., and Owen, J., Determination of Size Distribution of Macropores in Porous Materials—Macroporosity of Coke by Gas Flow Method: Anal. Chem., vol. 25, 1953, pp. 1222-1226.