Effect of Carbon Monoxide in Causing Nonuniform Gasification of Graphite by Carbon Dioxide

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Existing theories on the effect of mass transport on the rate (uniformity) of chemical reaction within a porous solid assume that the reaction is of integer order. However the carbon-carbon-dioxide reaction has the kinetic rate form, rate $= k_1 p_{CO_2}/(1 + k_2 p_{CO} + k_3 p_{CO_2})$. For conditions where the retarding effect of carbon monoxide is very pronounced, the buildup of small concentrations of carbon monoxide within the porous graphite can lead to appreciable nonuniformity of gasification. Thus the criteria normally used to predict uniformity of gasification break down. A numerical integration of the combined differential equation of mass transport and chemical reaction has been performed, with rate constants for the carbon-carbon dioxide reaction taken from the literature. The results indicate that extreme nonuniformity of reaction can exist even when the change in carbon dioxide concentration from the exterior of the sample to the interior is small. The results are similar to experimental determinations of nonuniformity of gasification, obtained by determining the porosity of reacted graphite samples as a function of depth from the reacting face. Experimentally nonuniformity of reaction was observed for gasification rates a hundredfold lower than the usual Thiele criteria would predict, probably because of carbon monoxide inhibition.

There is general agreement that the carbon-carbon dioxide reaction is retarded by its product—carbon monoxide (*1*). It is further shown that whether this retardation is caused by the chemisorption of carbon monoxide on active sites or by the reduction in the amount of surface-oxygen complex, the rate equation for carbon gasification, at conditions far from equilibrium, should be of the form

$$\text{rate} = k_1 p_{CO_2}/(1 + k_2 p_{CO} + k_3 p_{CO_2}) \quad (1)$$

Workers have confirmed experimentally that Equation (1) does describe the kinetics of the carbon-carbon dioxide reaction. Their results are summarized in Table 1. It is seen that there is a wide variation in the values for the rate constants, which perhaps can be explained by differences in the structure and purity of the carbons studied and lack of recognition of diffusion control. However in any case the data are in agreement that carbon monoxide strongly retards the gasification of carbon by carbon dioxide.

A previous publication by the authors (*1*) reported experimental results showing the nonuniform gasification of graphite by carbon dioxide. The usual criteria for predicting uniformity of gasification, which ignore product inhibition, were not consistent with the experimental results. It is the purpose of this paper to show that carbon monoxide inhibition, as given by Equation (1), can produce, under certain circumstances, substantial nonuniform gasification under conditions where the normal treatment of diffusional effects predicts negligible departure from uniformity of reaction.

No attempt will be made here to describe the experimental techniques or fully report the results, since this information is already in the literature (*1, 2*). In essence carbon samples 2 in. long by ½ in. diameter were reacted in 1 atm. of carbon dioxide in a flow system. Isothermal linear reaction rates were obtained for temperatures ranging from 900° to 1,350°C. Samples reacted to approximately 11% burn off at 925, 1,000, 1,200 and 1,305°C. were turned down in a lathe, with small incremental cuts, and the variation of porosity and BET area with radius determined. The variation of diffusion coefficient with porosity was also determined.

After Wicke (*3*) an attempt was made to explain the results with the relations developed for combined mass transport and integer order reactions (*1*). Two major anomalies were found. Firstly the Arrhenius plot of the results could not be explained by the usual criteria for entering the diffusion controlled zone. Secondly the variation of porosity through a sample reacted at 925°C. was markedly nonuniform, with the burnout at the exterior being almost twice as much as that in the interior. The criterion for the rate at the exterior of the sample to be no greater than 5% faster than the rate in the interior is

$$(R/C_R D)\, dw/dt < 0.1 \quad (2)$$

For the experimental conditions applying this gives a value of dw/dt of about 0.15 g. of carbon reacting per rod per hour. The experimental rate at 925°C. was 0.017. Thus the sample ought to have been almost uniformly reacted throughout its radius.

The apparent anomalies could not be explained by mass transport to the surface of the sample, by the variation of diffusion coefficient with porosity, or by replacing Fick's law by more exact forms of the mass transport equation for $C + CO_2 \rightarrow 2CO$. Temperature uniformity through a sample was investigated with the formula of Prater (*4*). When one considers the extreme case of high temperature reaction, with the concentration of the reactant being zero in the center of the sample, Prater's formula gave a temperature difference between the exterior and the interior of the sample of less than 1°C. With the highest value of apparent activation energy from the Arrhenius plot, 93 kcal./mole (*1*), a 1°C. temperature difference would give a variation in rate of less than 5%. At 925°C. the variation in rate from exterior to interior due to a temperature effect would be much less than this value of 5%, and consequently this effect cannot explain the experimental result.

The authors were forced therefore to re-examine the combined mass transport-chemical reaction equations bearing in mind that the reaction studied probably has a kinetic form approaching that of Equation (1), rather than being a zero, first-, or second-order reaction. [The authors accept Equation (1) only with qualification, because the experimental evidence for its applicability is not as strong as they would like and because the rate constants quoted by different workers show such a very large variation.]

RESULTS AND DISCUSSIONS

Consideration of Equation (1) shows that if k_2 is of comparable magnitude to k_3 and greater than 1, then the presence of carbon monoxide will have a significant retarding effect on the

TABLE 1. RATE CONSTANTS FOR THE CARBON-CARBON DIOXIDE REACTION

Type of carbon	Rate constants k_1	 k_2	 k_3
Coconut shell charcoal (6)	$10^{8.8}e^{-58.8/RT}$	$10^{-7.9}e^{45.5/RT}$	$10^{6.5}e^{-30.1/RT}$
Coal Coke (7)	$10^{4.8}e^{-47.9/RT}$	$10^{-1.9}e^{15.4/RT}$	$10^{-0.6}e^{6.4/RT}$
Coal Coke (8)	$10^{7.5}e^{-61.7/RT}$	$10^{-5.4}e^{40.3/RT}$	$10^{-1.5}e^{6.1/RT}$
Electrode carbon (9)	$10^{6.0}e^{-50.1/RT}$	$10^{-8.5}e^{60.6/RT}$	$10^{-0.8}e^{6.6/RT}$

reaction. When a porous material is reacting under conditions of internal diffusion control, the reactant concentration or partial pressure falls to almost zero in the interior. At the same time the product, carbon monoxide in this case, will build up in the interior, giving rise to further retardation of the reaction. The data of Table 1 show that the value of k_2 increases with decreasing temperature. Thus one might conceivably have a situation where at low temperatures and rates of reaction the fall in concentration of carbon dioxide from the exterior to the interior was only a few percent, but the corresponding build up of a few percent of carbon monoxide might cause considerable retardation of the reaction in the interior. The following section is a preliminary analysis of this possibility.

It is readily shown (5) that if rate Equation (1) applies, the steady state differential equation of combined chemical and internal mass transport effects is

$$d^2C/dr^2 + (1/r)\,dC/dr - (k_1C/D)/(1 + k_2C' + k_3C) = 0 \quad (3)$$

If the mass transport is mainly by Knudsen diffusion, then carbon monoxide has to diffuse out at twice the rate carbon dioxide diffuses in and

$$dC'/dr = -2dC/dr \quad (4)$$

If the external gas is carbon dioxide only, with a concentration C_R, and if negligible external mass transport effects are present, Equation (4) integrates to

$$C' = 2(C_R - C) \quad (5)$$

This may not be the exact relation of C to C', but one can say that at any radius in the sample a concentration of carbon dioxide exists plus a corresponding carbon monoxide pressure. The lower C is, the higher C' will be. Substituting Equation (5) into Equation (3) one obtains

$$d^2C/dr^2 + (1/r)\,dC/dr - (k_1C/D)/(1 + 2k_2(C_R - C) + k_3C) = 0$$

$$d^2C/dr^2 + (1/r)\,dC/dr - C/[(D/k_1)(1 + 2k_2C_R) + (D/k_1)(k_3 - 2k_2)C] = 0$$

or

$$d^2C/dr^2 + (1/r)\,dC/dr - C/(A + BC) = 0 \quad (6)$$

Obviously this equation will not behave like a simple integer order reaction except under certain limiting conditions. Furthermore one cannot use the normal criteria for this system. It is also clear that this is not a simple equation to solve and will probably have a series solution.

The main purpose at this stage was to determine whether the additional terms introduced by using rate Equation (1) have a pronounced effect on the normal mass transport criteria. Consequently it was decided to investigate the simpler system of a plane reacting at one face. It is easily shown that the differential equation to be solved in this case is

$$d^2C/dr^2 = C/(A + BC) \quad (7)$$

where the symbols have the same meaning as before, except that r is now the linear distance from the interior to the reacting face. A series solution gives a series in which the unknown constant cannot be conveniently evaluated in terms of the boundary condition. The equation was therefore integrated by a simple numerical procedure, with a finite difference technique employed.

To perform a numerical integration it is necessary to have the requisite kinetic data. With reference to Table

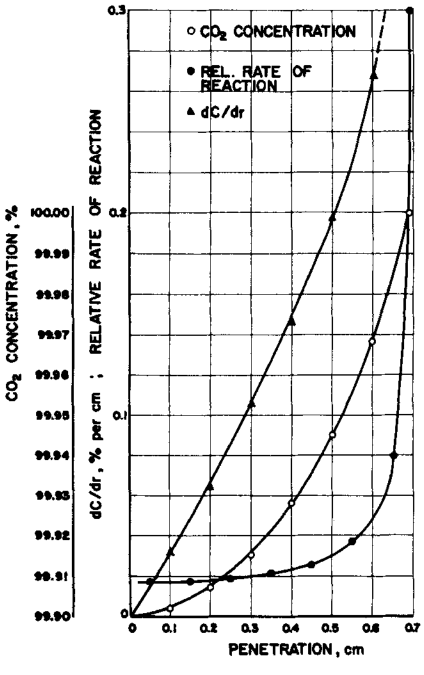

Fig. 1. Calculated reaction parameters within a plane of carbon reacted at 1,000°K.

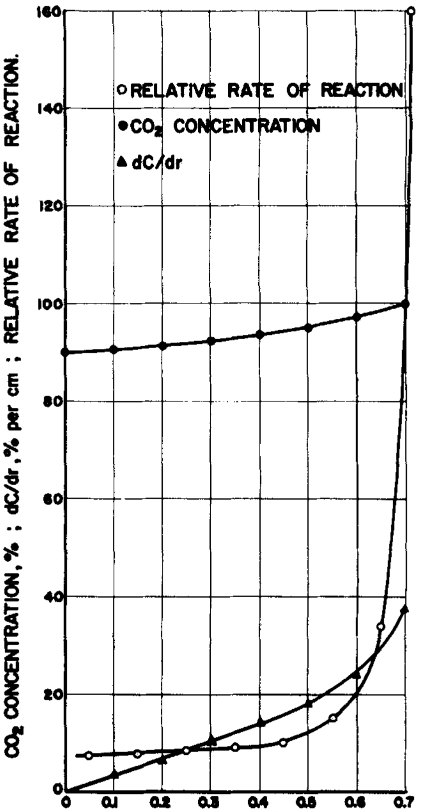

Fig. 2. Calculated reaction parameters within a plane of carbon reacted at 1,200°K.

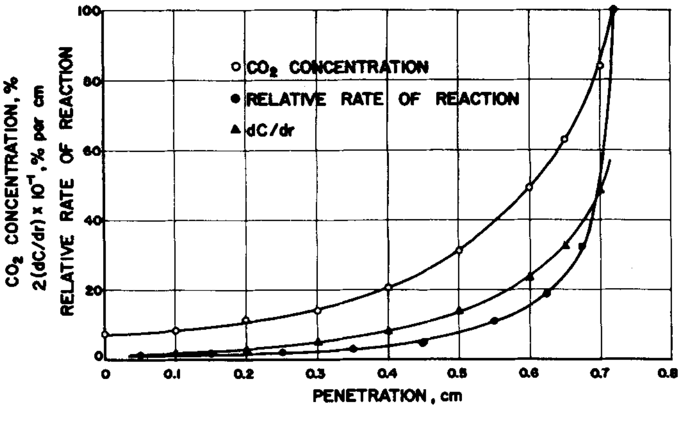

Fig. 3. Calculated reaction parameters within a plane of carbon reacted at 1,400°K.

1 the carbon most similar in properties to those possessed by the carbon used in this experimental work would be expected to be the electrode carbon. Therefore the quoted kinetic data for this material was used as given in Table 2. The other conditions chosen were: an external carbon dioxide pressure of 1 atm., $D = 0.1$ sq. cm./sec., $R = 0.7$ cm. With these figures and the rate data of Table 2, results were obtained as shown in Figures 1, 2, 3.

Figure 1 shows that at 1,000°K. the rates of reaction within the sample are very nonuniform even though the fall in carbon dioxide concentration from the exterior to the interior was only 0.1%. The normal diffusion criterion would predict that the sample would be well within the chemical reaction zone, with uniform reaction. At 1,200°K. the fall in carbon dioxide concentration was about 10%, giving a concentration ratio interior to exterior of 90%, but the ratio of specific rates between the interior and exterior was about 6%. Again the normal criterion would predict almost uniform burnout. At 1,400°K. the concentration ratio, interior to exterior, was 7.5% and the specific-rate ratio was about 2%. Thus at 1,400°K. the effect of carbon monoxide retardation is much less marked than at the lower temperatures. At 1,600°K. the rate data in Table 2 indicate that the effect of carbon monoxide retardation is relatively minor and the diffusion-controlled rate can be calculated with the normal criterion for a first-order reaction.

The porosity profiles obtained by the computation are much more nonuniform than the experimental values reported previously (*1*). There are two obvious reasons for this. Firstly the kinetic data were for a different carbon, with the electrode carbon appearing to be an extreme case as far as the effect of carbon monoxide retardation is concerned. Secondly the computed curves are based on the assumption of zero carbon monoxide concentration at the exterior of the carbon. Any build up of carbon monoxide on the exterior face due to mass transport limitations through the external boundary layer would give rise to greater uniformity of reaction through the sample. Carbon monoxide retardation of the reaction would be even more pronounced, but the difference in the retardation, interior to exterior, would be much less.

It is interesting to examine the Arrhenius plot corresponding to the computed data. The overall rates can be found by extrapolating the values of dC/dr to the exterior surface. That is

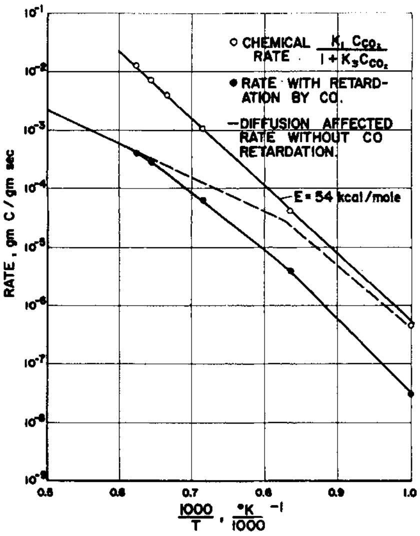

Fig. 4. Calculated Arrhenius plot for reaction in a plane 0.7 cm. thick.

$$\text{rate per sq. cm. of external surface} = D(dC/dr)_R \quad (8)$$

Figure 4 shows the Arrhenius curve. It can be seen that the low temperature results do not correspond to true chemical rates. If a reactant gas circulating system is used, similar to that used by Wicke, et al. (*3*), then it is possible that some carbon monoxide exists even at the exterior of the solid. If k_2 is large at low temperatures, rate Equation (1) will go to

$$\text{rate} = (k_1/k_2)p_{CO_2}/p_{CO} \quad (9)$$

The apparent activation energy would then be given by the ratio of activation energies for k_1 to k_2. From data for the electrode carbon used in the computation this would give an activation energy of 110.7 kcal./mole. The activation energy would change to that of k_1 alone at higher temperatures. Thus it is possible that the high activation energy at low temperatures found in reference *1* might be actually the composite of two rate constants rather than the true activation energy of a single rate-controlling step.

It should be emphasized that the authors have not proved that carbon monoxide retardation has a sufficiently great effect to explain the anomalies in their previously reported experim results. They have only shown that is possible that the deviations could be caused by carbon monoxide retardation. It is of little use to look for analytical solutions of Equation (6), or to program the numerical solution for a computer, until it has been demonstrated that retardation is a major factor. To do this accurate values of k_1, k_2, and k_3 at a series of temperatures are needed. The authors are at present determining reliable values of these rate constants for high purity carbons. Two different experimental techniques are being used so that rate data can be determined over a carbon dioxide pressure range of 1 mm. to 1 atm. Gross mass transport effects are avoided by the use of loosely packed powders or thin samples. The effect of carbon monoxide retardation due to small concentration gradients is avoided by having a known quantity of carbon monoxide present in the reacting gas, sufficient to overweigh concentration gradient effects. This work has progressed far enough to prove that carbon monoxide has a marked retarding effect for these high purity carbons. There are not as yet reliable values or activation energies for k_1, k_2, and k_3.

TABLE 2. RATE CONSTANTS FOR ELECTRODE CARBON (9)

Rate in g. C/g. C/sec.

$$= \frac{k_1 p_{CO_2}}{1 + k_2 p_{CO} + k_3 p_{CO_2}}, \ p \text{ in atm.}$$

T, °K.	k_1	k_2	k_3
1,000	0.236×10^{-5}	5.06×10^4	4.12
1,200	0.152×10^{-3}	316	2.54
1,400	0.0151	14.2	1.70
1,600	0.1448	0.50	1.26

CONCLUSIONS

An examination of the effect of carbon monoxide retardation on the carbon-carbon dioxide reaction shows that it is possible for this retardation to cause nonuniformity of reaction through a porous sample, even at low rates of reaction. It is believed that existing literature values (*6, 7, 8, 9*) of the rate constants of the reaction are not sufficiently reliable to use in determining the degree of this effect of carbon monoxide retardation and diffusion. On the other hand the measurements of rates and activation energy made by using thick beds or porous solid samples are also open to objection, since the effect of carbon monoxide retardation is not usually considered. It may be sufficiently large to give completely spurious results. These conclusions have led the authors to a program of work in which the three rate constants k_1, k_2, and k_3 are being measured at various temperatures, using high purity carbons and gases. It is hoped that future work on these rate constants will reconcile the conflicting activation energies at present available.

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TION

= concentration of carbon dioxide
C' = concentration of carbon monoxide
C_B = concentration of carbon dioxide in main gas stream
D = effective diffusion coefficient of carbon dioxide through porous graphite
k = rate constant
p = pressure
r = distance along radial direction of cylindrical sample
R = radius of cylindrical sample
T = temperature

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The Laminar-Turbulent Transition for Fluids with a Yield Stress

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The pumping of semifluid substances (that is substances which flow as fluids only when stressed beyond a finite yield stress) is of considerable practical interest in fields ranging from sewage treatment to nuclear reactor design. In many of these applications it is desirable to know the conditions which determine the onset of turbulent flow.

The onset of turbulent flow can be predicted quite accurately for the flow of Newtonian fluids in ducts of various geometries (*1*), and for the nonisothermal (*2*) and isothermal (*3*) pipe flow of non-Newtonian fluids characterized by the power-law rheological model. However in reference *2* it was shown that the treatment of data obtained with semifluid substances in terms of Metzner and Reed's (*4*) point slope technique did not permit the correlation of the flow transition data for these fluids. The purpose of the present paper is to compare the author's (*1*) method of predicting the laminar-turbulent flow transition with isothermal pipe-flow data for such semifluids and to present the theoretical equations for flow in other geometries.

THEORETICAL DEVELOPMENT

Pipe Flow

A rather general criterion for the onset of turbulence has been proposed (*1*) which, for the case of flow in straight pipes of circular cross section, may be written as*

$$K = \frac{1}{2}\,\frac{\rho}{dp/dz}\,\frac{d}{dr}\,(v_z^2) \qquad (1)$$

If Equation (1) is evaluated at $r = \bar{r}$, the radius at which the flow field is least stable (*1*) (obtained from the condition $dK/dr = 0$), and K is set equal to the constant (*1*) value $\kappa = 404$, one can solve for $\bar{v}_c$, the critical velocity of flow. This is usually most conveniently done in dimensionless form by expressing $\bar{v}_c$ as a Reynolds number.

In order to use Equation (1) an expression for $v(r)$ is required. Such an expression can be obtained by integration of the rheological equation of the fluid together with the equations of motion. A simple rheological equation for fluids exhibiting yield stresses is the linear Bingham (*5*) equation, which for cylindrical geometry is

$$\tau_{rz} = \pm\,\tau_o - \eta\,\frac{dv_z}{dr} \qquad (2)$$

when $|\tau_{rz}| > |\tau_o|$. If $|\tau_{rz}| \leqq |\tau_o|$, the rheological equation is $dv_z/dr = 0$. In Equation (2) η is the plastic viscosity or coefficient of rigidity, and τ_o is the yield stress.

From Equation (2) and the equation of motion the following expressions for the velocity profile can be obtained:

$$v(\xi) = \frac{\tau_w r_w}{2\eta}\,[1 - 2\alpha\,(1-\xi) - \xi^2]; \quad \alpha \leqq \xi \leqq 1 \qquad (3)$$

$$v(\xi) = \frac{\tau_w r_w}{2\eta}\,(1-\alpha)^2; \; 0 \leqq \xi \leqq \alpha \qquad (4)$$

where $\xi = r/r_w$ is a dimensionless radius and $\alpha = \tau_o/\tau_w = r_o/r_w$ is the dimensionless radius of the unsheared plug in the central core of the flow field. From Equations (3) and (4) the average velocity can be obtained as

$$\bar{v} = \frac{\tau_w r_w}{4\eta}\left(1 - \frac{4}{3}\alpha + \frac{1}{3}\alpha^4\right) \qquad (5)$$

which is the familiar Buckingham (*6*) equation.

From the nature of the flow field and the stability parameter (*1*), it is evident that $\alpha < \bar{\xi} < 1$, where $\bar{\xi}$ is the point of minimum stability. Therefore from Equations (1) and (3) one can obtain

$$\bar{\xi} = \alpha + (1-\alpha)\sqrt{1/3} \qquad (6)$$

From Equations (1), (3), (5), and

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* The relation between Equation (1) and a similar parameter proposed by Ryan and Johnson (*3*) is discussed in reference *1*.