Subscripts and Superscripts

$( )^*$ = dimensional variable
$( )_{sep}$ = separation

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Kinetics of High-Temperature Carbon Gasification Reaction

A simple technique is developed and is used to measure simultaneously the overall rate and the depth of the reaction zone in the porous solid. It is shown that by using some simple models, one may calculate the intrinsic rate constant and the pore diffusivity from the overall rate and the penetration depth. Models which allow for a varying pore diffusivity according to a linear porosity profile are presented, and have been shown more satisfactory than the constant diffusivity models of Thiele and of Zeldovich when applied to the high temperature carbon-carbon dioxide reaction.

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SCOPE

For solid-catalyzed and most of gas-solid reactions in a porous solid, the overall reaction rate is determined by the pore diffusion rate and the chemical reaction rate. When the chemical rate is sufficiently lower than the pore diffusion rate, there is no significant concentration drop within the solid and the entire solid particle is efficiently used. On the other hand, when pore diffusion is relatively slow, the reaction is limited to within a zone on the exterior surface, which we shall call penetration depth. Many rigorous theoretical and experimental results have been published for the former case. Some of the models, such as the early ones by Thiele and by Zeldovich, may be extended to describe the kinetics for the latter case.

Most of the gas-carbon reactions under commercial conditions (i.e., at high temperatures) belong to the diffusion-controlled regime. To study the kinetics in this regime, it is much easier to measure the overall rate and the penetration depth, rather than measuring the chemical rate and the pore diffusion rate. Knowing the overall rate and the penetration depth, one may obtain information on the chemical rate and pore diffusion rate through modeling. Much experimental work has been done on measuring the penetration depth of gas-carbon reactions in the high temperature range, primarily by Golovina et al., for the C-CO_2 reaction at temperatures up to 3400 K.

In this work, a simpler and more accurate technique is developed to measure the penetration depth, which also provides data for the overall rate simultaneously. We also present kinetic models which allow for porosity and surface area variations, and hence the diffusivity variation, within the reaction zone.

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CONCLUSIONS AND SIGNIFICANCE

A new technique has been developed and used successfully to measure simultaneously the overall rate and the penetration depth for the C-CO_2 reaction in the temperature range 1300–1600°C. From these data, it is shown that the first-order rate constant and the pore diffusivity can be calculated using the simple models proposed here. The models allow for variations of pore diffusivity according to a linear porosity in the reaction zone. The rate constants (at 1,300°C) predicted by these models agree reasonably well with the experimental value of k. The values predicted by the models of Thiele and of Zeldovich are too high.

The rise of the intrinsic rate constant with temperature is slowed down in this temperature range (with activation energy of 35 kcal) from that below this range (with activation energy of 74 kcal), and it peaks between 1500 to 1600°C. The pore diffusivity is proportional to $T^{1.05}$ in this temperature range for the carbon sample. The value of $\epsilon^2 D_g$, as assumed in some recent models, is too high for the effective pore diffusivity by a factor between 74 to 80 in the temperature range. The value predicted by the dusty gas model, assuming that the micropores do not limit the flux, is too high by a factor between 60 to 65. Furthermore, it is shown that the gas film diffusion controlled regime does not exist for the C-CO_2 reaction.

In this study, we are concerned with the kinetics of gas-solid reaction in the regime where the overall rate is severely limited by the pore diffusion rate. All gas-solid reactions enter this regime when the temperature is sufficiently high, unless there is a phase change in the solid. For reactions in this regime, knowledge of the penetration depth of the gaseous reactant(s) is critically linked to the understanding of the overall rate. It is also of practical importance as it relates to the effect of particle size on the overall rate. This was the problem of direct concern to Zeldovich (1939). The particular problem which Zeldovich addressed concerned a carbon gasification reaction. In the meantime, the same problem of diffusion with reaction was studied by Damkohler and by Thiele with regard to solid catalyzed reactions. Recent reviews on the solid catalyzed reactions may be found in Butt (1980), Carberry (1976), Aris (1975), and Smith (1970). For the noncatalyzed gas-solid reactions, the situation may be much more complicated when there are solid products, or "ash layer," formed upon reaction. In this case, the "structural" models are needed to account for the rates. Szekely et al. (1976) have reviewed these models published prior to 1976. The shrinking-unreacted-core models have been discussed in detail by Wen and coworkers (1970). For the noncatalyzed gas-solid reactions with only gaseous products, the problem becomes similar to the solid-catalyzed reactions, except that there is a changing pore size distribution for the noncatalyzed reactions, either with respect to time or with respect to distance from the exterior surface. The problem of most practical importance in this category is the carbon gasification or combustion reaction. Indeed, many significant papers have been published on the subject. A very brief review in the context of this work will be given here.

The variation of rate of the gas-carbon reactions with temperature has been classified into three zones by Wicke (Walker et al., 1959), from chemical control in Zone 1 (at low temperatures) to gas-film diffusion control in Zone 3 (at high temperatures). The transition from Zone 1 to Zone 2 occurs at about 900–1200°C. The majority of the published work has been done for reactions in Zone 1, although the higher-temperature reactions are of more practical importance. Models for the Zone-1 kinetics are available (Petersen, 1957; Hashimotto and Silveston, 1973; Dutta and Wen, 1977; Lee, 1980; Bhatia and Perlmutter, 1980; Srinivas and Amundson, 1980; Gavalas, 1980). In most of the models, a constant effective diffusivity, D_e, was assumed. The others assumed that D_e is equal to $\epsilon^2 D_g$.

Our recent studies on pore diffusion in graphite at temperatures up to 700°C showed that the ϵ^2 dependence is indeed a good one, but $\epsilon^2 D_g$ is much too high as compared with the measured values of D_e (Yang and Liu, 1981) and in fact, D_e could be lower by two orders of magnitude (Liu, 1980).

For gas-carbon reactions in the high-temperature range, the gaseous reactants can only penetrate into the pores for a short distance. The penetration depth contains the information on the pore diffusion rate, the chemical rate, and the gas film diffusion rate. Knowledge of this depth clearly can be extremely useful in understanding the interplay of the individual rate steps. Indeed, the penetration depth has been the subject of measurements by Walker and coworkers (Austin and Walker, 1963; Walker et al., 1959) and by Golovina et al. (1973; 1974). In their work, the partially reacted carbon was shelled in layers and the surface areas (or densities) of the layers were measured. From the profile, the penetration depth was calculated which corresponded to the depth where the surface area approached the bulk value. The extensive work done by the Russians showed that the depth was about constant (at about 200 μm) over a temperature range from 1700°K to 3400°K, and as the temperature was decreased from 1700°K, the depth increased rapidly. In light of the results regarding the substantial penetration depth, one would question that, in "Zone 3," if the gas film diffusion is limiting the rate, or, does "Zone 3" exist for gas-carbon reactions?

Results of two major studies are to be presented here. First, a simple gravimetric technique is developed for measuring the penetration depth. Secondly, models similar to the Thiele-Zeldovich model are developed to show the interplay of pore diffusion, surface reaction and the penetration depth. These models have included the strong dependence of pore diffusivity on the changes of porosity into the solid. The usefulness of the value of the penetration depth is also shown.

IMPROVED MODELS FOR SOLID WITH CHANGING POROSITY

The basic assumptions for the models are: (1) first-order surface reaction; (2) equimolar counter diffusion; and (3) linear porosity profile. Regarding the specific surface area, S_v, two cases will be considered. In the first model, S_v will be assumed constant and an analytical solution is obtained. Next, S_v will be expressed as a function of porosity, ϵ, according to the Petersen model (1957) and the model will be solved numerically.

The bases of the three assumptions and their applicabilities will now be addressed, with respect to the high-temperature gas-carbon reactions.

For all gas-carbon reactions in the high-temperature range, the surface rates approach the first-order form because the desorption terms become negligible in the Langmuir-Hinshelwood rate expressions. The assumption of equimolar counter diffusion can be met under two circumstances. The first is when there are equal number of moles of gaseous reactants and products. The second is not straight-forward, which is when the mole fraction of the gaseous reactant is low. As shown previously (Yang and Liu, 1981), by starting from a modified Stefan-Maxwell flux equation (with effective binary pore diffusivities replacing the gas-phase diffusivities) with low mole fractions of reactant (A) and product (B) in an inert gas (C), the flux of A can be approximated as

$$N_A = -\frac{C_T D_{AC}}{1 + y_A}\frac{dy_A}{dx} \tag{1}$$

which can be further simplified to

$$N_A = -C_T D_{AC}\frac{dy_A}{dx} \tag{2}$$

This approximation indicates that the diffusive flux predominates the convective flux when the mole fraction of the carrier gas is high. The third assumption is the linar porosity profile. This assumption was made based on the published experimental data on the porosity profiles of partially reacted carbon (e.g., p. 184 in Walker et al., 1959). The data showed that, in the high temperature range, the porosity profile is virtually a straight line except that it curves into the bulk value toward the bottom of the penetration depth. Thus, the following porosity profile is assumed:

$$\epsilon = ax^* + b \tag{3}$$

where $b = 1$ and $a = \epsilon_o - 1$, and x^* is the dimensionless distance to be defined shortly. We shall now proceed with the derivation of the model with a constant S_v.

In making a mass balance for the gaseous reactant A, we further assume that the quasi-steady state prevails, and adopt a plain geometry, i.e., the solid being a flat plate. We have

$$-\frac{dN_A}{dx} = kS_vC_A \tag{4}$$

where both S_v and C_A are based on per unit bulk volume, and x is the distance from the surface.

The effective diffusivity is approximated as, based on our previous study on high-temperature pore diffusivity (Yang and Liu, 1982)

$$D_e = \frac{D_g}{\lambda}\epsilon^2 \tag{5}$$

Combining Eqs. 2, 4 and 5, we have

$$\epsilon^2\frac{d^2y^*}{dx^{*2}} + 2\epsilon\frac{d\epsilon}{dx^*}\frac{dy^*}{dx^*} - \frac{kh^2S_v}{Dg/\lambda}y^* = 0 \tag{6}$$

where

$$y^* = y/y_o = yC_T/C_{Ao}$$
$$x^* = x/h$$

with the boundary conditions

$$x^* = 0, \quad y^* = 1 \tag{7}$$

$$x^* = 1, \quad y^* = 0.01 \tag{8}$$

$$x^* = 1, \frac{dy^*}{dx^*} = 0 \tag{9}$$

The second boundary conditions states that the concentration of carbon dioxide at the reaction zone/unreacted carbon interface is 1% of the surface concentration (analogous to the boundary layer theory).

Using the linear porosity profile (Eq. 3), the governing equation becomes

$$(ax^* + b)^2\frac{d^2y^*}{dx^{*2}} + 2a(ax^* + b)\frac{dy^*}{dx^*} + Ay^* = 0 \tag{10}$$

$$A = -kh^2S_v\lambda/Dg \tag{11}$$

An analytical solution exists if the following is satisfied (Arfken, 1966)

$$\frac{A}{a^2} < \frac{1}{4} \tag{12}$$

Since A is negative, this condition is always met. The solution is given by

$$y^* = M(ax^* + b)^p + N(ax^* + b)^q \tag{13}$$

where

$$p,q = \frac{1}{2}(-1 \pm \sqrt{1 - 4A/a^2}) \tag{14}$$

The values of M,N and p can be obtained by satisfying the three boundary conditions (Eq. 7, 8 and 9). As mentioned, the value of a is also known from the initial porosity, ϵ_o. The value of b is unity because the porosity at the exterior surface is assumed unity.

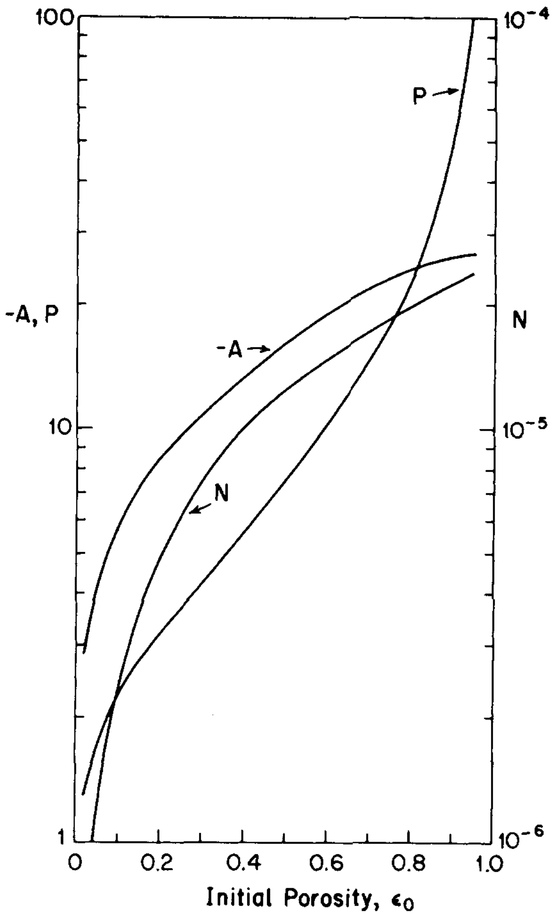

Figure 1. Parameters in the analytical solution.

Substituting the boundary conditions, Eqs. 7–9, into Equations 13 and 14, one can solve the set of simple algebraic equations for the constants M, N, p and q. For a given gas-solid reaction, the values of these four constants depend only on ϵ_0. The values of N, p and A are plotted versus ϵ_0 as shown on Figure 1. The value of M is related to N by

$$M + N = 1 \tag{15}$$

The value of q may be calculated with Eq. 14.

A significant result is that, for a given gas-solid reaction, the value of A is fixed, and which is only related to ϵ_o as shown in Figure 1. The dimensionless group A has a similar meaning as does the Thiele modulus. Knowing A, one may calculate the penetration depth if k and D_e are known.

With the concentration profile (Eq. 13) known, we may calculate the overall rate with the following equation

$$\frac{dm}{dt} = -D_e\frac{y_{Ao}P}{RT\,h}\frac{dy^*}{dx^*}\bigg|_{x^*=0} \tag{16}$$

The ideal gas law is assumed here. The overall rate, dm/dt, is expressed as moles of reactant A per time and is based on per unit exterior surface area. Note that the rate is expressed in terms of D_e. By using Eq. 5 and the value of A, one may also express dm/dt in terms of k only.

As an example of applying these results, we use the carbon gasification reaction, which will be described fully later. The carbon material had an initial porosity of 17.7%. From Figure 1,

$$-A = \frac{kh^2S_v\lambda}{Dg} = 8.04 \tag{17}$$

From Figure 1 and Eq. 14, one obtains the values of the constants in Eq. 13. The overall rate is

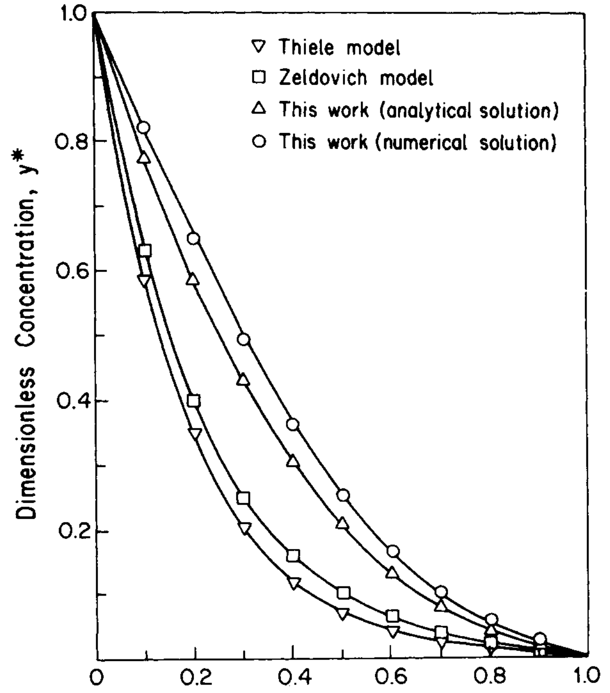

Figure 2. Concentration profiles predicted by models.

$$\frac{dm}{dt} = 2.45\,\frac{y_{Ao}PD_{eo}}{RT\,h} \tag{18}$$

The rate may also be expressed in terms of k as follows

$$\frac{dm}{dt} = 0.305\,\frac{Py_{Ao}khS_v}{RT} \tag{19}$$

Equations 18 and 19 relate the overall rate and the penetration depth with k and D_e.

Comparison with Other Models

The above results will be compared with the classic models of Zeldovich and of Thiele, both assumed a constant effective diffusivity in the porous mass. The two models are similar except in their boundary conditions. As a result, Zeldovich obtained an exponential concentration profile whereas Thiele's solution is near exponential.

In order to compare their models with the present one, we introduce the following condition in their solution:

$$\frac{C_A}{C_{Ao}} = 0.01 \text{ at } x = h \tag{20}$$

Zeldovich Model

The concentration profile in the Zeldovich model is

$$C_A = C_{Ao}\exp\left[-x\sqrt{\frac{kS_v}{D_e}}\right] \tag{21}$$

Substituting Eq. 20 into Eq. 21, we have

$$\frac{kh^2S_v}{D_e} = 21.2 \tag{22}$$

The rate per unit experior surface in moles of A per unit time is, from the flux at the exterior surface,

$$\frac{dm}{dt} = 4.6\,\frac{D_ey_{Ao}P}{RT\,h} \tag{23}$$

From Eqs. 22 and 23,

$$\frac{dm}{dt} = 0.22\,\frac{Py_{Ao}khS_v}{RT} \tag{24}$$

Equations 23 and 24 relate the overall rate and penetration depth with k and D_e. D_e here is a constant, and may assume the value at the mean porosity in the reaction zone.

Thiele Model

The concentration profile in this model is (assuming $dC/dx = 0$ at h)

$$\frac{C_A}{C_{Ao}} = \frac{e^{m(h-x)} + e^{-m(h-x)}}{e^{mh} + e^{-mh}} \tag{25}$$

Using the definition of penetration depth (Eq. 20),

$$\frac{kh^2S_v}{D_e} = 28.1\ (= m^2h^2) \tag{26}$$

The rate per unit exterior surface in moles of A per unit time is

$$\frac{dm}{dt} = 5.30\,\frac{Py_{Ao}D_e}{RT\,h} \tag{27}$$

or

$$\frac{dm}{dt} = 0.189\,\frac{Py_{Ao}khS_v}{RT} \tag{28}$$

A comparison of the concentration profiles of the three models is shown on Figure 2. This comparison shows simply that the effect caused by the higher diffusion rate toward the exterior surface in our model. Further comparisons of these models, along with the following model with varying porosity and surface area, will be discussed in the light of our experimental results.

Model with Varying Porosity and Surface Area

In the first model, the assumption of constant surface area and a linear porosity profile in the reaction zone was made in order to obtain an analytical solution to Eq. 6. In the following analysis, we will relax the assumption of constant surface area to obtain a numerical solution. These two models will then be compared, along with the models by Thiele and by Zeldovich.

In relating the surface area with the local porosity, we may use the Petersen model (1957). The porosity profile is assumed to be linear as before.

$$\epsilon = (\epsilon_0 - 1)x^* + 1 \tag{29}$$

The pore radius is related with ϵ by

$$\left(\frac{r}{r_o}\right)^3 - G\left(\frac{r}{r_o}\right)^2 + \frac{\epsilon}{\epsilon_o}(G-1) = 0 \tag{30}$$

where G is a geometric factor of the pore structure and may be obtained from ϵ_o by the following equation

$$\frac{4}{27}\epsilon_oG^3 - G + 1 = 0 \tag{31}$$

The surface area profile is given by

$$S_v = \frac{\epsilon_o}{r_o}\left(\frac{r}{r_o}\right)\left[\frac{2G - 3(r/r_o)}{G-1}\right] \tag{32}$$

Equation 32 gives a zero surface area at the exterior surface of the pellet where the porosity is assumed to be one. To solve Eq. 6, an iteration procedure is necessary, which is outlined in the following.

A parabolic concentration profile is first assumed to begin the iteration. The rate constant corresponding to the concentration profile is given by

$$\frac{dm}{dt} = khy_{Ao}P\int_o^1 y^*S_v\,dx^* \tag{33}$$

Thus, all the parameters in Eq. 6 may be computed, and a numerical solution to Eq. 6 is obtained (Appendix). With this new concentration profile, the rate constant k is reevaluated. Iterations

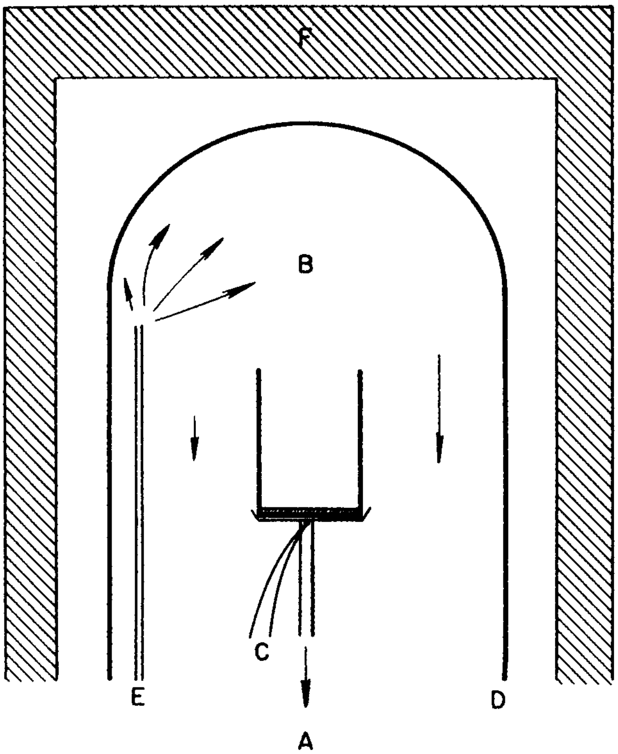

Figure 3. Schematic of experimental apparatus: *A*, to automatic recording balance; *B*, gas flow; *C*, thermocouple (Pt-10% Rh/Pt); *D*, alumina bell jar; *E*, alumina bleeder; *F*, high-temperature furnace.

are carried out until the concentration profile matches the solution of Eq. 6.

The value of D_e at any distance x_1^* may also be computed by equating the flux at x_1^* with the rate beyond that point as shown in the following equation.

$$-\left(D_e \frac{dy^*}{dx^*}\right)_{\text{at } x_1^*} = kh^2 \int_{x_1^*}^{1} y^* S_v \, dx^* \qquad (34)$$

Using this model, one may calculate the rate constant k and the local diffusivity, D_e (at x_1^*), from measured data on dm/dt and h. The values of dm/dt and h can be measured simultaneously in a single experiment with our simple technique described as follows.

NEW TECHNIQUE FOR MEASURING PENETRATION DEPTH

The previous technique for measuring penetration depth involves the measurement of the surface area or density profile in the partially reacted carbon rod or sphere. The sample is carefully shelled into thin layers and the surface areas of the successive layers are measured. The point at which the surface area approaches the bulk value is taken as the bottom of penetration depth. Using this technique, Golovina et al. (1973, 1974, 1980) have done extensive studies on the high-temperature kinetics of gas-carbon reactions. The penetration depth of CO_2 in a graphite has been measured by them at temperatures ranging from 1,500 to 3,400 K and pressures ranging from 1 to 40 atm. The depth was near a constant level at each pressure in the temperature range of 1,700–3,100 K, being higher outside this range. This constant penetration depth varied from 100 to 350 μm, increasing with pressure.

The technique developed in this work is based on the diffusion cell method (Yang and Steinberg, 1977), which is similar to the one originated by Stefan for measuring vapor diffusivity (Lee and Wilke, 1954; Sherwood and Pigford, 1952). It should be mentioned that a technique similar to this one was applied for studying the combustion rate of carbon by Davis and Hottel (1934). (This paper was kindly pointed out to us by Professor R. H. Essenhigh of Ohio State University.) The main advantage of using the diffusion cell method to study high temperature kinetics is that the gas film resistance is well controlled, and thereby leaving us only pore diffusion and chemical rate to disentangle.

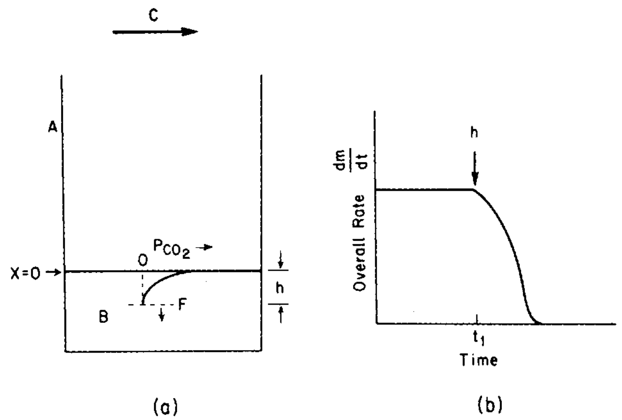

Figure 4. Illustration of penetration depth (*h*) measurement. (a) Schematic of diffusion cell: *A*, cell; *B*, carbon disk; *C*, bulk gas flow; P_{CO_2}, CO_2 concentration profile; *F*, advancing front. (b) Location of *h* in typical rate measurement.

The method of measuring the penetration depth using the diffusion cell is illustrated on Figures 3 and 4. Figure 3 shows the apparatus used. Figure 4 shows the principle for measuring the penetration depth. A thin carbon disk or pellet is placed on the bottom of the cell (size: 1.6 cm diameter × 2.4 cm depth). A gas flow (CO_2 in argon) is swept over the cell. The overall rate, as measured gravimetrically, is recorded. A typical result of the rate is shown on Figure 4b. After an initial period (which is not shown in the figure), the rate is constant. This is due to the quasi-steady state established in the system; both in the cell path and in the porous carbon. At time t_1, the rate starts decaying. The time t_1 corresponds to the point when the penetration depth, h, of the gaseous reactant is equal to the thickness of the remaining disk. One way to measure h is to stop the reaction at t_1 (by shutting off CO_2 in the flow) and measure with a micrometer. From this measurement, one obtains both the steady rate (dm/dt) and the penetration depth. This technique is obviously much simpler, more accurate, and less time-consuming than the previous one.

In applying this technique, one must make sure that the reactant gas does not diffuse around the edge of the disk and react beneath the disk. This was checked in this work by using an open cylinder (with no bottom) twice the length of the cell, instead of the cell. The carbon disk was placed in the middle of the cylinder (being cemented with Sauerisen high temperature cement on the wall), and the overall rate was measured. In all cases, the overall rate doubled the rate measured with the cell. This result assured us that only the upper surface of the disk was responsible for the rate and h.

EXPERIMENTAL

The apparatus was identical with the one used previously, which included a Mettler Differential Thermoanalyzer and a gas handling system (Yang and Steinberg, 1977). The diffusion cell was an alumina cup (16 mm diameter and 24 mm depth). The bulk gas flow contained 8.33% CO_2 in argon and was kept at 1 atm pressure. The carbon sample was a high purity nuclear-grade graphite (H-451). A typical sample disk had a diameter slightly below 16 mm, a thickness of about 0.11 cm, and weighed about 0.4 g. Other materials and the procedure for rate measurement were the same as described in the earlier work.

A more pore size characterization of the graphite has been given elsewhere (Yang and Liu, 1979). The graphite had a bimodal pore distribution with ϵ_i = 4.0% consisting pores with radius centered at 50 Å, and ϵ_a = 13.7% consisting pores with radius at about 1,000 Å. The subscripts i and a denote micropore and macropore, respectively. The chemical analysis of the graphite was also given (Yang and Steinberg, 1977).

TABLE 1. EXPERIMENTAL DATA FOR THE CARBON-CARBON DIOXIDE REACTION

Temperature, °C	1,300	1,400	1,500	1,600
Exterior Concentration (y_{Ao}), atm	0.037	0.030	0.022	0.022
Overall Rate (dm/dt), mg/cm²/min	1.43	1.55	1.57	1.50
Penetration Depth (h), μm	270	196	150	155

RESULTS AND DISCUSSION

With the simple experimental technique developed in this study, we have measured simultaneously the penetration depth and the quasi-steady state, overall rate. Using the models, one can readily calculate the two important parameters: the intrinsic rate and the effective pore diffusivity. In the following, we will present our experimental data (on h and dm/dt) for the C-CO$_2$ reaction in the temperature range of 1,300–1,600°C and the calculated first-order rate constant and the effective diffusivity. The values of k and D_e were calculated by using the four models discussed in the foregoing, and were compared. A clear improvement is seen in our simple models over the Thiele model and the Zeldovich model for the reaction system studied here. Finally, we will address the question of the existence or non-existence of Zone III in heterogeneous reactions, and establish a simple and qualitative criterion on its existence.

Penetration Depths and Overall Rates

Before presenting the data, we first estimate the maximum temperature effects caused by the endothermic reaction. This can be done, as shown previously (Yang and Steinberg, 1977), by making a heat balance assuming conduction is the only mode of heat transfer, and calculating the ΔT between the reacting layer and the alumina sample holder where temperature was measured. The maximum ΔT calculated was 0.05°C, which eliminated doubts about our temperature measurements as well as any possible thermal diffusion flux in the stagnant path above the carbon surface.

The experimental data are shown in Table 1. The bulk stream concentration of CO$_2$ in Ar flowing over the cell was 0.083 atm in all experiments. The exterior surface concentrations on the carbon disk were calculated (following Yang and Steinberg, 1977), and shown in Table 1. The overall rates and the penetration depths are also shown. At temperatures below 1,300°C, e.g., at 1200°C, the rates dropped sharply and the reaction soon entered the kinetically controlled regime (or Zone 1). These data are not included in this discussion.

The penetration depths were measured with a micrometer by stopping the reaction at the onset point of the rate decay which is easily identifiable. The value of h increased rapidly below 1400°C toward lower temperatures, but approached a steady value at higher temperatures. These data agreed with the data published by Golovina (1980) using a different graphite. However, the large scattering in her data (ca. 50–70 μm) is eliminated in this technique because the measurement in this technique is more accurate and much simpler.

Surface Rate

The data on dm/dt and h'are then used to calculate k and D_e.

First, the assumptions made in the models are to be justified for the reaction. The C-CO$_2$ reaction is approximately first order with respect to CO$_2$ in the temperature range of this work (Walker et al., 1959). The mole fraction of the reactant $A(y_A)$ was below 4% in the reaction zone in all cases studied here. With the two assumptions satisfied, we will use the four models to calculate for k and D_e.

The values of k and D_e are listed in Table 2. In order to compare these values, and hence to evaluate the models, one needs to compare with experimentally determined values. The intrinsic rate

TABLE 2. RATE CONSTANT AND DIFFUSIVITY CALCULATED FROM OVERALL RATE AND PENETRATION DEPTH

Temperature, °C	1,300	1,400	1,500	1,600
Thiele Model				
D_e, 10^{-2} cm²/s	0.84	0.89	0.97	1.01
k, 10^{-3} cm/s	3.49	6.99	13.05	12.75
Zeldovich Model				
D_e, 10^{-2} cm²/s	0.97	0.99	1.12	1.16
k, 10^{-3} cm/s	3.03	5.9	11.33	11.07
This Work, Analytical (constant S_v)				
D_e, (at $\bar{\epsilon}$), 10^{-2} cm²/s	1.49	1.54	1.72	1.79
k, 10^{-3} cm/s	2.35	4.20	8.06	7.90
This Work, Numerical				
D_e (at $\bar{\epsilon}$), 10^{-2} cm²/s	1.91	1.97	2.20	2.29
k, 10^{-3} cm/s	2.15	4.05	7.65	7.52
Experimental (Liu, 1980)				
k, 10^{-3} cm/s	1.82			

constants (k_1, k_2 and k_3) of the reaction in the Langmuir-Hinshelwood rate equation have been measured by Liu (1980) with the same carbon sample. However, the temperature in his experiments ranged only up to 1,245°C, because above this temperature pore diffusion resistances became significant with the smallest particle size he could obtain. From the reactivation energy (74 kcal/mole) of his data, we extrapolated the k_1 values (which is k in our case) to 1,300°C, and obtained: $k = 1.82 \times 10^{-3}$ cm/s. Further extrapolations (above 1,400°C) would not be meaningful because the intrinsic reactivity of carbon is known to slow down from the exponential rise with temperature; and in fact, it peaks at 1,500 to 1,600°C (Rosner, 1972; Yang and Steinberg, 1977).

Comparing the k value from Liu's experimental data with the k's calculated from the models, it is encouraging to see that our models yield the closest value to the experimental value. The k values are further shown on Figure 5. This figure also shows clearly the reactivity peaking phenomenon of carbon surface. The above comparison indicates that the models by Thiele and by Zeldovich predict higher intrinsic reactivities for a given set of overall rate and penetration depth. The reason for this is that the

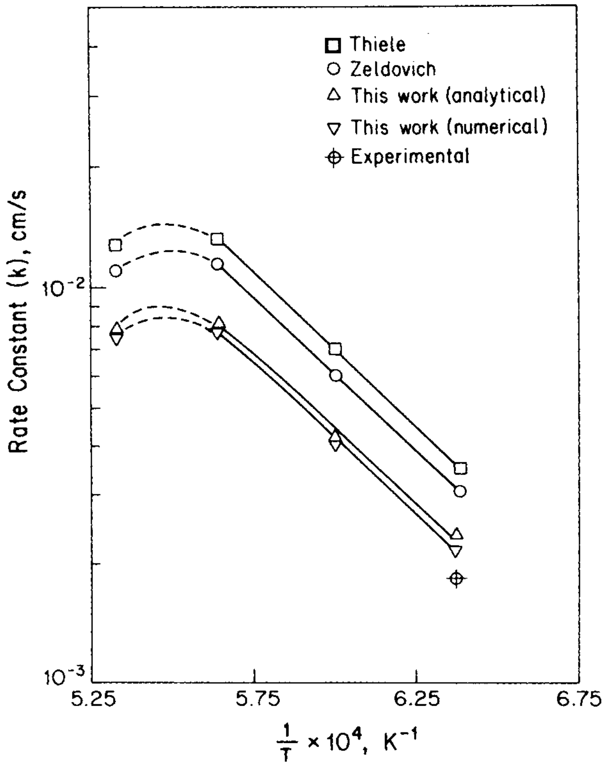

Figure 5. Rate constants calculated from models and compared with experimental value.

TABLE 3. EFFECTIVE PORE DIFFUSIVITIES IN THE UNBURNT CARBON

Temperature, °C	D_e (This Work), 10^{-3} cm^2/s	D_e (Dusty Gas), 10^{-2} cm^2/s	τ	$\epsilon^2 D_g$, cm^2/s
1,300	1.35	8.69	64	0.10
1,400	1.39	9.06	65	0.11
1,500	1.56	9.43	61	0.12
1,600	1.63	9.77	60	0.13

concentration is lower throughout the reaction zone for these two models, as seen in Figure 2. It is also interesting to compare the numerical model with the analytical model, for the k values. The numerical model appears to yield k values closer to the experimental data. But the improvement is rather small. The improvement achieved by allowing varying pore diffusity is rather substantial, as seen in Figure 5. The improvement made by allowing a varying surface area, i.e., the numerical model versus the analytical model, is rather small.

The activation energy for the surface reaction in the temperature range of 1,300 to 1,500°C is approximately 35 kcal/mole, which is much lower than that in the lower temperature range reported by Liu (1980).

Effective Pore Diffusivity

The basic difference between the previous models and our models is that we allow for a varying pore diffusivity in the reaction zone. In the models of Thiele and of Zeldovich, a constant diffusivity is used. From the data on h and dm/dt, the values of D_e are calculated and listed in Table 2. The D_e's for the Thiele and Zeldovich models may be regarded as the D_e evaluated at the mean porosity, $\bar{\epsilon}$. For comparison, we used our models to calculate D_e also at $\bar{\epsilon}$. The D_e's from our models are higher than that from the two previous models.

The temperature dependence of D_e calculated from the models is approximately $T^{1.05}$. This dependence is in good agreement with the very scarce published data on pore diffusion at elevated temperatures (Yang and Liu, 1982).

It is thought to be interesting to compare the D_e values calculated from our rate data with the values predicted from the available models for predicting D_e based on the pore structure. To do this, we use the relatively simple dusty-gas-model, keeping in mind that this model is by no means the best one for porous carbons. To use the dusty-gas-model, one needs to know the pore structure. The only pore structure information we have is for the unburnt carbon, or at the end of the reaction zone where the porosity is 17.7%. We further assume that only the macropores contribute to diffusion, and the micropores are the branches or dead-end pores. The porosity for the macropores was 13.7%, with pore radius of 1,000 Å. The D_e predicted with this branched pore structure will be the upper limit of the D_e. If some or all of the micropores are involved in fluxes, the D_e values should be substantially lowered. To use the dusty gas model (Scott and Dullien, 1962), we have

$$D_e = \frac{\epsilon D_g}{\tau} \ln \left[\frac{1 - \alpha y_{A2} + D_g/D_k}{1 - \alpha y_{A1} + D_g/D_k}\right] \ln \left[\frac{1 - \alpha y_{A2}}{1 - \alpha y_{A1}}\right] \qquad (35)$$

$$\alpha = 1 + N_B/N_A \qquad (36)$$

Here, the values of y_{A2} and y_{A1} are taken as 0.03 and 0, respectively, and N_B/N_A is the negative square root of the ratio of molecular weights of CO_2 and Ar. The dusty-gas D_e's are listed in Table 3. Here, D_e is taken from our previous work (Yang and Steinberg, 1977) and D_k is for the 1,000 Å radius pores. The D_e calculated from our analytical solution, based on 17.7%, is also shown in the table. The tortuosity, τ, is rather constant over the temperature range. The high tortuosity indicates that the branched pore structure assumed here is not adequate; some of the micropores must be in series with the macropores. In the series structure, the micropores serve as bottle necks and thereby substantially lower the effective diffusivity. In this connection, a tortuosity of 26 was calculated for a large-pore graphite sample previously (Evans et al., 1961).

TABLE 4. RESISTANCES IN REACTION ZONE AND IN GAS FILM

Temperature, °C	$1/k_g$, (s/cm)	$1/(0.128\, kh\, S_v)$, (s/cm)
1,300	0.75	0.61
1,400	0.68	0.43
1,500	0.61	0.29
1,600	0.56	0.29

In recent modeling studies, it has been often assumed that $D_e = \epsilon^2 D_g$. Here, the tortuosity was assumed to be $1/\epsilon$. To clarify this point, we have also listed the $\epsilon^2 D_g$ values in Tables 3. The error introduced by using this assumption is that such values are too high by a factor of 74 to 80 for the porous carbon in the temperature range of 1,300° to 1,600°C.

Nonexistence of Zone 3 Kinetics

So far we have analyzed the interplay between pore diffusion and chemical reaction in the reaction zone. It is thought to be interesting to also briefly address the question of the gas-film diffusion resistance as compared with the combined resistance in the reaction zone. From such an analysis, we will be able to see if "Zone 3" indeed exists for the carbon gasification reaction.

The overall rate in the reaction zone as derived from our analytical model may be rewritten in terms of concentration as follows.

$$\frac{dm}{dt} = 0.28\, C_{Ao} k S_v h \qquad (37)$$

The flux through the gas film is

$$\frac{dm}{dt} = k_g (C_{Ab} - C_{Ao}) \qquad (38)$$

Combining Eqs. 37 and 38, we have

$$\frac{dm}{dt} = \frac{C_{Ab}}{\dfrac{1}{k_g} + \dfrac{1}{0.128\, khS_v}} \qquad (39)$$

The mass transfer coefficient, k_g, is defined as D_g/δ, where δ is the thickness of the stagnant gas film. Under the reaction conditions in this work, δ is the depth of the diffusion cell which is much greater than normal flow conditions in reactors. Nonetheless, the two resistances in Eq. 39 are compared in Table 4. From this comparison, it is clear that the two resistances are comparable and that "Zone 3" does not exist. As the temperature is further increased, the gas film resistance will continue to decrease whereas the resistance in the reaction zone becomes rather constant, as evidenced by Golovina's data (1980). Thus, it may be concluded that "Zone 3" does not exist for the C-CO_2 reaction for carbons with a reasonable porosity.

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NOTATION

a,b = porosity constants defined by Eq. 3
A = dimensionless group defined by Eq. 11
C_A = concentration of reactant gas A (g mole/cm^3)
C_{Ab} = bulk value of C_A
C_{Ao} = value of C_A at exterior surface
C_T = total concentration of gases (g mole/cm^3)
dm/dt = overall rate per unit exterior surface area (g mole/cm^2/s)
D_{AC} = porous diffusivity of A in C (cm^2/s)

D_e = effective diffusivity in pores (cm^2/s)
D_{eo} = D_e at exterior surface
D_g = gas phase diffusivity (cm^2/s)
D_k = Knudsen diffusivity (cm^2/s)
G = geometric constant of the porous structure defined by Petersen (1957)
h = depth of reaction zone or penetration depth (cm or μm)
k = first-order rate constant (cm/s)
k_g = mass transfer coefficient across stagnant film (cm/s)
m = $(kS_v/D_e)^{1/2}$ ($cm^{-1/2}$)
M,N,p,q = constants in Eq. 13
N_A = flux of reactant gas (g mole/cm^2/s)
r,r_o = pore radius and initial pore radius (cm)
P = total pressure (atm)
R = gas constant
S_v = surface area per bulk volume (cm^2/cm^3)
t = time
T = absolute temperature (K)
x = distance from the exterior surface (cm)
x^* = dimensionless distance (x/h)
y or y_A = mole fraction of reactant gas
y_o or y_{Ao} = value of y at experior surface
y^* = dimensionless concentration (y/y_o)
y_{A2}, y_{A2} = mole fractions at two ends of a porous material
α = net flux parameter defined by Eq. 36
$\epsilon,\epsilon_o,\bar{\epsilon}$ = total porosity, initial porosity and mean porosity, respectively
λ = constant defined by Eq. 5
τ = tortuosity factor

APPENDIX: NUMERICAL SOLUTION

Equation 6 may be rewritten as

$$\frac{d^2y^*}{dx^*} + \frac{2}{\epsilon}\frac{d\epsilon}{dx^*}\frac{dy^*}{dx^*} + \frac{Ay^*}{\epsilon^2} = 0 \quad \text{(A1)}$$

The central difference approximations of the derivatives are

$$\frac{d^2y^*}{dx^{*2}} = \frac{y^*_{i+1} - 2y^*_i + y^*_{i-1}}{\Delta x^{*2}} + \text{truncation error of } \Delta x^{*2} \text{ order} \quad \text{(A2)}$$

$$\frac{dy^*}{dx^*} = \frac{y^*_{i+1} = y^*_{i-1}}{2\Delta x^*} + \text{error } (\Delta x^{*2}) \quad \text{(A3)}$$

Substituting Eqs. A2 and A3 into Eq. A1 and rearranging, we have

$$\left[1 - \frac{\Delta x^*}{\epsilon_i}\frac{d\epsilon_i}{dx^*}\right] y^*_{i-1} + \left[\frac{A\,\Delta x^{*2}}{\epsilon_i^2} - 2\right] y^*_i + \left[1 + \frac{\Delta x^*}{\epsilon_i}\frac{d\epsilon_i}{dx^*}\right] y_{i+1} = 0 \quad \text{(A4)}$$

or,

$$A_i y^*_{i-1} + B_i y^*_i + C_i y^*_{i+1} = D_i \quad \text{(A5)}$$

This is a set of algebraic equations taking values of i from 2 to $I_{\max} - 1$. Substituting the boundary conditions (Eqs. 7 to 9) into Eq. A5, the constants A, B, C and D may be determined at the boundaries.

$$\text{For } x^* = 0,\ y^* = 1,\ i = 1,$$

$$B_1 = 1,\ C_1 = 0 \text{ and } D_1 = 1$$

$$\text{For } x^* = 1,\ y^* = 0.01,\ i = I_{\max}$$

$$A_{I_{\max}} = 0,\ B_{I_{\max}} = 1 \text{ and } D_{I_{\max}} = 0.01$$

The set of Eq. A5 forms a tridiagonal matrix which can be solved with standard techniques (Roache, 1970).

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