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i = refers to species number
 j = refers to reaction number
 t = refers to total moles

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Rate of Diffusion-Controlled Reaction Between a Gas and a Porous Solid Sphere

Reaction of SO₂ with CaCO₃

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The reaction rate is assumed to be governed by two diffusional processes: the diffusion of SO₂ through the pores, and the diffusion of SO₂ through a layer of solid reaction product which forms on the active solid surface progressively as the reaction proceeds. One or the other predominates, depending on particle size, gas composition, and temperature. The theory accounts qualitatively for the observations of Borgwardt (1970) and Coutant *et al.* (1970).

One of the major sources of atmospheric pollution in the United States is the coal-fired power plant, which frequently consumes sulfur-laden fuel and produces flue gas containing a few thousand parts per million SO₂. In recent years there has been increasing interest in chemical processes for the removal of sulfur compounds from the flue gas stream. Many of these involve treatment of the effluent gas stream from the plant with alkaline liquid reagents in large scrubbers before the gas is discharged. Such processes are capable of nearly complete recovery of gaseous sulfur but the equipment may be very costly and may be hard to add to many existing power plants. A process which can be applied to existing plants involves the injection of finely powdered limestone or Dolomite into the fire box of the boiler, where the solid particles decompose, forming calcium oxide. This reacts with sulfur dioxide and with excess oxygen, forming calcium sulfite and calcium sulfate. The reaction product must be collected with the fly ash in dust collection equipment.

In the evaluation of the limestone injection processes, it is necessary to know the rates of the chemical reactions between the gas and the solid in order to determine the quantity of

solid required, its particle size, the temperatures at the injection point and downstream, and the time of exposure of the solid to the gas. Previous studies of the rate phenomena have led to somewhat confusing results.

Borgwardt (1970) measured the rates of reaction using beds of solid particles of CaO through which the gas passed. His times of exposure were on the order of one to two minutes, much longer than those which are of practical interest. He assumed that the heterogeneous reaction rate was governed by the speed of a chemical reaction and evaluated an apparent first-order rate constant, which he reported varied with the particle size and with the elapsed time of the reaction. Such ambiguous results are cause for caution in the application of his data.

Coutant *et al.* (1970) carried out a more extensive and realistic series of experiments at the Battelle Memorial Institute, in which particles of limestone (type 2061, screened to average size of about 0.00895-cm diameter) were injected into a current of hot gas which flowed upward through an insulated tube. By varying the height of the particle injection point, various times of exposure could be obtained, from a fraction of a second to about three seconds. The particles were collected and analyzed to determine the extent to which

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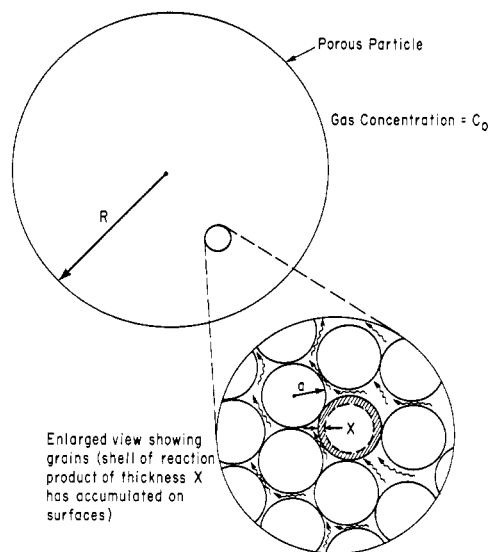


Figure 1. Drawing of a porous, reactive particle containing grains of solid reagent

conversion to CaO and to CaSO_3 and CaSO_4 had occurred. The gas concentration of SO_2 varied between 0.0004 and 0.009 mole fraction and the temperature between 1600° and 2148°F . Interpretation of the data was attempted using an equation apparently borrowed from classical corrosion theory, according to which the quantity of sulfur picked up should be proportional to the square root of the reaction time. Thus the rate was expected to vary inversely with $t^{1/2}$, evidently because of the changes in thickness of a layer of reaction product through which SO_2 had to diffuse to reach the active reagent underneath. It was noted, however, that several of the sets of data did not follow such a relationship and it was not possible to find a systematic relationship between the "rate constants" and gas composition, temperature, or particle size. Thus, application of the data to a variety of conditions may be difficult on the basis chosen.

The idea that the rate of the reaction is governed by diffusion is an appealing one and some aspects of the Battelle data suggest that the idea may be correct. For example, at comparable times or extents of reaction the rates did not appear to vary with temperature as rapidly as would be expected from typical chemical reaction activation energies. Moreover, the plots of amount of sulfur absorbed vs. time were concave toward the time axis, as in most diffusion-controlled processes in which the buildup of concentration inside the particle reduces the driving force, or the accumulation of a reaction product increases the resistance. Nevertheless, the process could not be represented as an ordinary linear diffusion problem because the rate did not seem to be proportional to the gas concentration.

A diffusion-plus-reaction mechanism which suggests itself as potentially capable of accounting for the data is one in which a particle of solid is assumed to be made up of many smaller spherical particles of solid reagent, as indicated by the sketch in Figure 1. The sulfur dioxide diffuses through the pores separating these subparticles and reacts on their surfaces. The speed of the reaction is determined by the thickness of a solid reaction product layer which forms on the surface of each subparticle and by the local concentration inside the pores. The product layer thickness is, in turn, determined by the whole time history of the local concentration since it represents the accumulated product—i.e., the integral of the

local reaction rate at the particular position in the porous solid. Note that it is not necessary to assume that the SO_2 dissolves in the sulfite or sulfate layer for such a layer could easily develop cracks or fissures owing to a mismatch of solid density with the calcium oxide underneath.

Such a reaction mechanism is not wholly different from the simple one assumed by Coutant et al.; it is a logical extension of theirs, including an additional pore diffusion process which may be important if gaseous diffusion is slow, if the specific surface of the pores is large, or if the particles are large. Under these conditions the composite particles should react principally near their exterior surfaces, their interior regions being inaccessible to SO_2 .

The theory is also similar in many respects to one introduced earlier by Szekeley and Evans (1970) as their "grain model." The new theory is different, however, in one major respect. The theoretical calculations of Szekeley and Evans and of Sohn and Szekeley (1972) assume that the porous solid particles are comprised of "grains" of uniform size but the rate of the reaction on the surface of these grains is assumed to be proportional to the local concentration of the gaseous reactant and not retarded appreciably by diffusion through the developing shells of solid product. As a result, the diffusion equations are linear in the internal gas concentration, and the rate of uptake of the gaseous reagent by the porous particles is predicted to be proportional to the concentration of the reagent in the bulk of the gas. As will be shown, data indicate that the effect of the concentration driving force is not always linear, suggesting that nonlinear reaction rate terms are needed in the diffusion equations.

Very likely there are reaction systems in which rates of the chemical steps are important, as suggested by Shen and Smith (1965), but an advantage of the chemical reaction rate-free, combined diffusion theory is that it yields a comparatively simple solution containing only two independent combinations of physical properties and dimensions. Thus, applying it to the interpretation of rate data is comparatively simple. When the derived values of physical properties obtained in this way are physically reasonable and when the calculated effects of variables such as time of exposure, particle size, and gas concentration are satisfactory, as they prove to be for the sulfur dioxide-limestone system, the diffusion theory represents a simple, superior alternative.

Theory of Diffusion plus Reaction Between a Gas and a Porous Solid Sphere

Consider the material balance representing the transient diffusion of a gas having concentration $C(r,t)$ through the pores of a spherical particle of radius, R , reacting on the surface of the pores at a rate v per unit surface, as in Figure 1. Let the internal surface area per unit volume of the particle be S_p . The equation which results is

$$\left(\frac{D\alpha}{\tau}\right) \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r}\right) = \frac{\partial C}{\partial t} + S_p v \quad (1)$$

in which α represents the fraction by volume of pores, τ is their tortuosity, and D is the gaseous diffusivity.

The local reaction rate, v , can be computed by considering the diffusion of gaseous reactant through a spherical shell of reaction product of thickness X which forms on the surface of each subparticle of solid reagent. We assume that such diffusion processes are always at steady state, and we evaluate the diffusion flux in the following equation by multiplying the solid-phase diffusion coefficient, D_s , by the geometric-

mean cross-sectional area and the quotient of concentration difference by film thickness:

$$\rho_s 4\pi(a - X)^2 \left(\frac{dX}{dt} \right) = \frac{D_s}{X} 4\pi a(a - X) C(r, t) \quad (2)$$

If the gaseous reactant must dissolve in the surface of the reaction product layer we should include a Henry's law coefficient as a factor on the right multiplying the solid diffusion coefficient; if the gas diffuses through cracks in the product layer the coefficient would be omitted. Equation 2 is an ordinary differential equation from which $X(r, t)$ can be found as a function of the subparticle radius, a , the physical properties of the solid, and the local value of the integral of C with respect to time.

To find an expression for $v(r, t)$, we need to solve explicitly for X , in order to evaluate the diffusion flux into the subparticle,

$$v(r, t) = \frac{a - X}{aX} D_s C(r, t) \quad (3)$$

It is difficult to obtain a simple expression for v except when the thickness of the product layer is small compared with the subparticle radius—i.e., only when the fractional conversion of the solid is small. Then we may take $X \ll a$ and find

$$X^2 = (2 D_s / \rho_s) \int_0^t C(r, p) dp \quad (4)$$

and

$$v(r, t) = \left(\frac{D_s \rho_s}{2} \right)^{1/2} \frac{C(r, t)}{\left(\int_0^t C(r, p) dp \right)^{1/2}} \quad (5)$$

Introducing this result into Equation 1 and setting $c = C/C_0$, $\theta = \beta t$, and $\xi = r/R$, we obtain

$$\nabla_{\xi}^2 c = \left(\frac{\tau R^2 \beta}{D \alpha} \right) \left(\frac{\partial c}{\partial \theta} \right) + \frac{S_V \tau R^2}{D \alpha C_0} \left(\frac{D_s \rho_s C_0 \beta}{2} \right)^{1/2} \frac{c}{\left(\int_0^{\theta} c(\xi, p) dp \right)^{1/2}} \quad (6)$$

Now it is very likely that for the conditions of real interest the time-derivative term on the right will be insignificantly small, as in the classical problem of the effectiveness factor for a porous catalyst particle. We shall drop the term by assuming that $\tau R^2 \beta / D \alpha \ll 1$, an assumption which we can justify a posteriori. (Its greatest value was 0.0007 for the data quoted below.) Now, if we choose

$$\beta = \frac{2 C_0 D^2 \alpha^2}{D_s \rho_s S_V^2 \tau^2 R^4} \quad (7)$$

our mathematical problem reduces to

$$\frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left(\xi^2 \frac{\partial c}{\partial \xi} \right) = \frac{c}{\left(\int_0^{\theta} c d\theta \right)^{1/2}} \quad (8)$$

with the boundary conditions

$$c(1, \theta) = 1; c_{\xi}(0, \theta) = 0; c(\xi, 0) = 0 \quad (9a, b, c)$$

Note that Equation 8 is not linear; as a result, we can expect that the gas concentration will appear in a nonlinear way in the solution. In fact, the characteristic time, β^{-1} , depends on the ratio of solid and gas molar concentrations. After we

Table I. Numerical Values of Reaction Rate and Fraction Conversion from Diffusion Theory

$\theta = \beta t$	Dimensionless rate at $\xi = 1, \frac{\partial c}{\partial \xi}(1, \theta)$			Dimensionless total quantity, absorbed, $\gamma F = \int_0^{\theta} c_{\xi}(1, p) dp$		
	c_{ξ}	$\theta^{1/4} c_{\xi}$	$\theta^{1/2} c_{\xi}$	γF	$\theta^{-3/4} \gamma F$	$\theta^{-1/2} \gamma F$
0	∞	1.287		0	1.717 ^a	
0.02	3.174	1.193		0.0879	1.65	
0.04	2.475	1.106		0.1435	1.606	
0.05	2.273	1.075		0.1683	1.592	
0.10	1.728	0.971		0.2666	1.589	
0.15	1.462	0.909		0.3447	1.430	
0.20	1.292	0.864		0.4144	1.382	
0.30	1.081	0.799		0.5322	1.310	
0.40	0.9517	0.757		0.6335	1.260	
0.50	0.8603	0.723		0.7239	1.218	
0.60	0.7911	0.696		0.8063	1.182	
0.70	0.7362	0.673		0.8825	1.151	1.056
0.80	0.6933	0.656		0.9540	1.128	1.067
1.00	0.6244	0.624	0.624	1.0855	1.085	1.085
1.2	0.5733	0.600	0.628	1.205	1.050	1.100
1.5	0.5160	0.5613	0.621	1.368		1.117
∞						1.188 ^a

^a By extrapolation.

have obtained the solution, we shall want to find the instantaneous rate of passage of SO_2 across the exterior surface of the sphere, given by

$$N = \frac{\alpha D C_0}{\tau R} \left(\frac{\partial c}{\partial \xi} \right) (1, \theta) \quad (10)$$

where $N(t)$ is the rate per unit of external surface area. Then, we shall want to compute the fraction of the total solid reagent contained in the particle which has been consumed at any time of exposure, F :

$$F = \frac{3}{R \rho_s (1 - \alpha)} \int_0^t N dt = \gamma^{-1} \int_0^{\theta} c_{\xi}(1, p) dp \quad (11)$$

where

$$\gamma = \frac{2 D \alpha (1 - \alpha)}{3 R^2 S_V^2 \tau D_s} = \frac{R^2 \rho_s \tau (1 - \alpha)}{3 D C_0 \alpha} \beta \quad (12)$$

The solution of Equation 8 is presented in the Appendix. Table I gives a few selected values of numerical results, including values of the instantaneous dimensionless rate, $(\partial c / \partial \xi)(1, \theta)$, and the cumulative dimensionless fraction conversion $\int_0^{\theta} c_{\xi}(1, p) dp$, vs. dimensionless time, θ . Note that, for small θ , the instantaneous rate is very nearly proportional to $\theta^{-1/4}$ and the reaction fraction is proportional to $\theta^{3/4}$; for large θ , the corresponding relationships are $\theta^{-1/2}$ and $\theta^{1/2}$, respectively. Thus, the theory provides a gradual transition from a situation at small θ , in which the reacting region of a particle is near its surface and very little SO_2 reaches the center, to a different situation at large θ , in which the SO_2 is spread nearly uniformly through the pores and all the particle's interior reacts. Large θ therefore corresponds to the situation assumed by Coutant et al. (1970), and the calculated time dependence agrees with their assumption.

Figure 2 shows how the ratio of SO_2 concentrations at the center and the surface of the porous particle depends upon θ . Figure 3a is a plot of the instantaneous rate and Figure 3b shows the cumulative fraction reacted.

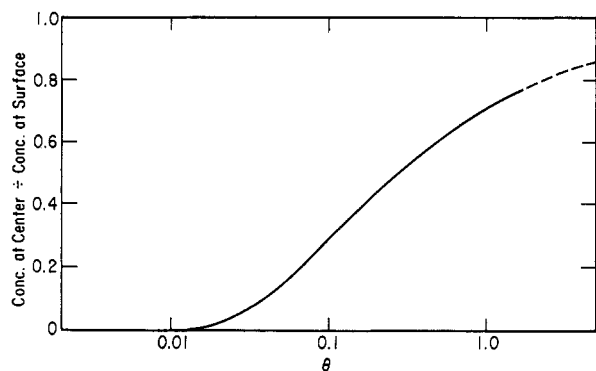


Figure 2. Depletion of gaseous reactant at center of sphere owing to diffusional resistance in pores

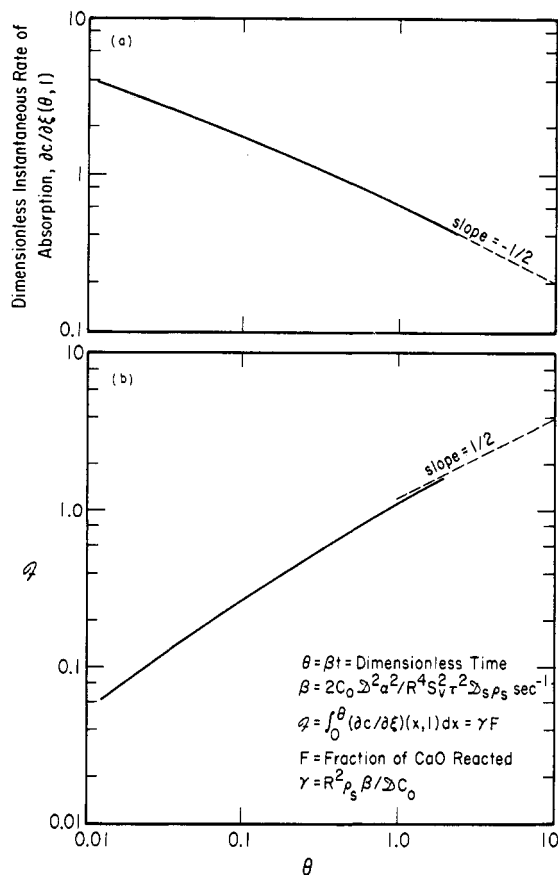


Figure 3. Theoretical values of rate of transport across exterior surface and fraction conversion of solid

Variation with time of exposure

When the original expression for the rate of absorption is evaluated with the theoretical results, we obtain

$$4 \pi R^2 N = 13.6 (\alpha^{1/2} D_s^{1/2} D_s^{1/4} S_v^{1/2} \rho_s^{1/2} R^2 C_o^{3/4} / \tau^{1/2} t^{1/4}) \quad (13)$$

when pore diffusion is controlling at small θ and

$$4 \pi R^2 N = 5.5 (D_s^{1/2} S_v \rho_s^{1/2} R^3 C_o^{1/2} / t^{1/2}) \quad (14)$$

when the diffusional resistance of the pores is small and θ is large. Note that depending on the time constant, β , the dependence of the rate on particle size can change from R^2 to R^3 , the effect of gas concentration from $C_o^{3/4}$ to $C_o^{1/2}$, and the effect of exposure time from $t^{-1/4}$ to $t^{-1/2}$, respectively. Moreover, the effect of temperature, presumably contained in D and D_s and possibly also in S_v , can also vary.

Under the assumption of small conversion, which we have made, the only effect of the size of the tiny subparticles is through the specific surface as expressed by

$$S_v = 3 (1 - \alpha) / a$$

The assumption, which has led to simple mathematical results, is not an essential one. If conditions leading to $F \rightarrow 1$ are important, Equations 1-3 can be solved numerically. Under these conditions one additional parameter, a/R , would affect the results for large θ .

Interpretation of Data of Borgwardt (1970) and Coutant et al. (1970)

The diffusion theory contains two combinations of physical constants, β and γ , defined in Equations 7 and 12. Each contains several quantities, such as the specific surface area and the solid diffusion coefficient, which are difficult to estimate and which must be found from the data themselves. Note, however, that the combination β/γ contains constants that are readily accessible from independent measurement or can be estimated approximately.

$$\frac{\beta}{\gamma} = \frac{3 D C_o \alpha}{R^2 \rho_s \tau (1 - \alpha)} \quad (15)$$

When we assume that gas diffusivity in the pores is equal to its bulk value, which varies with the $^{7/4}$ power of the absolute temperature, and take $\alpha \sim 0.5$ and $\tau \sim 1.0$,

$$\beta/\gamma = 2.29 \times 10^{-4} (y/R^2) (T/273)^{3/4}, \text{ sec}^{-1} \quad (16)$$

where y is the mole fraction of SO_2 in the gas, R is in cm, and T is in $^\circ\text{K}$. Obviously if α is smaller than 0.5 and τ is larger than unity, β/γ can be smaller. In the following, however, a value found from Equation 16 will be referred to as a "standard value."

The procedure for estimating the remaining parameter from the data, either β or γ , is to compute β/γ from Equation 16 (or from the same equation with a multiplying constant) and to determine β so as to minimize deviations from the theory. If βt is sufficiently small, it will be possible to determine β by dividing each of the measured values of the fraction conversion, F , by $t^{3/4}$, taking an average value of the quotient, and referring to Table I to find the appropriate value of $\gamma F/\theta^{3/4}$ in the expression

$$F/t^{3/4} = [\theta^{-3/4} \gamma F] (\beta/\gamma) \beta^{-1/4} \quad (17)$$

from which $\beta^{-1/4}$ and β can be computed. Similarly, if βt is sufficiently large, an equation like Equation 17 will give a value of $\beta^{-1/2}$. One sees that, following this procedure, the data at large values of $C_o t/R^4$, corresponding to large θ , should give a more reliable value of β and of the constants it contains, such as D_s and S_v .

Note also that by choosing β/γ smaller than its "standard value," one can reduce the value of β to be found, causing the time dependence of the rate to be more nearly as $t^{-1/4}$ than as $t^{-1/2}$ and also changing the effects of R and C_o , as indicated in Equations 13 and 14. Thus, when data are available for various gas compositions and various particle sizes, as well as for varying times of exposure, it may be possible to find best values of both γ and β when all the data are considered. In general, the problem is one of nonlinear curve fitting because of the changing functional behavior of the two constants, as shown in Table I.

Effect of Particle Size on Reaction Rate

Figure 5 shows the data of Borgwardt (1970) plotted logarithmically as suggested by the diffusion theory. Note that the

Table II. Values of Physical Constants Derived from Data of Borgwardt—Effect of Particle Size

(Constants based on the "standard value" of β/γ from Equation 16)

Particle diam., cm	Derived constants		βt at av t	βR^4 , $\text{sec}^{-1} \text{cm}^4$	γR^2 , cm^2
	β , sec^{-1}	γ			
0.0096	14	156	820	7×10^{-9}	3.6×10^{-3}
0.025	0.6	48	37	15×10^{-9}	7.5×10^{-3}
0.13	6×10^{-4}	1.3	0.035	11×10^{-9}	5.5×10^{-3}
			Av	11×10^{-9}	4.1×10^{-3}

If $\alpha = 1/2$, $\tau = 1$, $a = 40 \mu$, it follows that $D_s = 4 \times 10^{-7} \text{cm}^2/\text{sec}$.

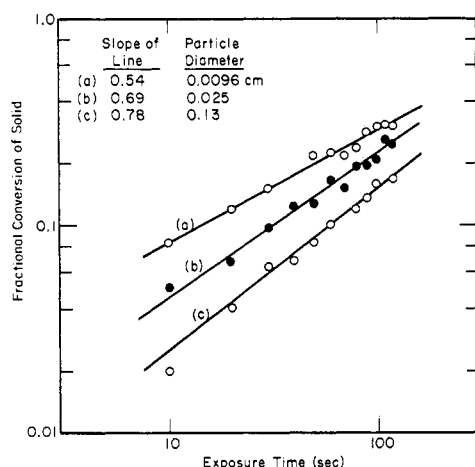


Figure 4. Effect of exposure time and particle size on conversion of calcium oxide

Data of Borgwardt (1970)

straight line drawn through the points representing the smallest particles has a slope just greater than $1/2$, suggesting that for these particles there was not much difference in the SO_2 concentration at the center and at the surface and negligible diffusional resistance in the pores. The data for the largest particles, however, yield a slope approximately equal to $3/4$, suggesting that these particles were large enough for their centers to be ineffective. The instantaneous rates of reaction, dF/dt , can be evaluated easily as a function of t and particle size. The results show that the rate at constant t is proportional to the -0.29 power of diameter at $t = 10$ sec and to the -0.18 power at $t = 60$ sec. These numerical results should be associated with the intermediate particle size. The slope would be 0 if all the interior of each particle were reacting equally and equal to -1 if there were major resistance to diffusion through the pores, as indicated in Equations 13 and 14. Evidently, particles about a quarter of a millimeter in diameter experience some influence of pore diffusion.

By fitting the theoretical results to the Borgwardt data and using Equation 16 to evaluate β/γ , we obtain the results shown in Table II. The values of βt corresponding to $t = 60$ sec, the average time of exposure, show that only for the largest particles was there appreciable pore diffusion resistance. The last two columns in the table show that the derived values β and γ vary with particle radius approximately in the way expected from the theory.

Although it is possible to determine the product $S_v^2 D_s \sim 40 \text{sec}^{-1}$ from the empirically derived values of either β or γ ,

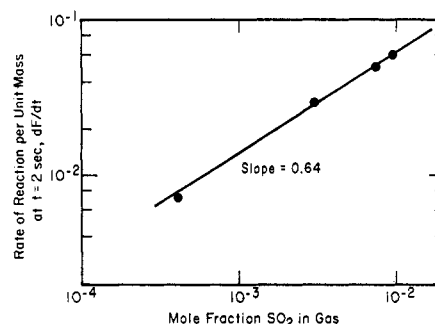


Figure 5. Effect of concentration of SO_2 on rate of reaction with limestone

Data of Coutant et al. (1970)

Table III. Values of Physical-Constant Groups, β and γ , Derived from Data of Coutant et al. (Battelle) Using "Standard Value" of β/γ (Equation 16)

Mole fraction SO_2 in gas	Gas temp, $^{\circ}\text{F}$	β , Sec^{-1}	β/γ	γ	βt_{av}
A. Effect of Gas Composition					
0.0004	1692	0.32	800	23	0.55
0.00302	1692	6.0	2000	58	8.2
0.00748	1690	12.3	1600	48	19.7
0.00954	1703	16.2	1700	49	25.8
		Av	1500	45	
B. Effect of Temperature					
0.00303	1600	8.2		81	
0.00302	1692	6.0		58	
0.00277	1845	2.5		25	
0.00305	2041	3.3		28	
0.00302	2109	6.9		57	
0.00306	2148	16		130	

Note: $\beta = 2 C_o D^2 \alpha^2 / D_s \rho_s S_v^2 \tau^2 R^4$, $\beta = 2 D \alpha (1 - \alpha) / 3 D_s S_v^2 \tau^2 R^2$

when we use estimated values of α and τ , neither S_v nor D_s can be determined separately. Nevertheless, if the pure guess is made that the elementary subparticles were about 40μ in diameter and $\alpha \sim 1/2$ and $\tau \sim 1$, D_s turns out to be about $10^{-6} \text{cm}^2/\text{sec}$. Obviously this is a highly unreliable value because it is highly sensitive to the assumed value of a . If a were off by a factor of 10, D_s would be changed by a factor of 100.

Moreover, the values of β computed from the data are strongly affected by the assumed ratio of the true value of (β/γ) to its "standard value" according to Equation 15. A nonlinear least-squares procedure applied to the same data shows that the quality of fit of the data can be improved by taking β/γ equal to 0.11 times its nominal value, yielding smaller values of $R^4 \beta$ and $S_v^2 D_s = 5000 \text{sec}^{-1}$, corresponding to $D_s \sim 10^{-5} \text{cm}^2/\text{sec}$ if $a \sim 40 \mu$.

The value of such highly speculative estimates lies in the possibility of attaching significance to the assumptions made in the derivations of the rate equations. Since none of the diffusivities estimated above for the penetration of the layer of product CaSO_4 by SO_2 are as small as expected for diffusion in the solid state, it seems possible that the diffusional process in the accumulating layer of product is assisted by cracks or fissures.

Effect of Gas Concentration of SO_2 on Reaction Rate

The data of Coutant et al. (1970) were taken at gas concentrations ranging from 0.0004 to 0.0095 mole fraction SO_2

Table IV. Physical Properties of Solid Particles Found by Fitting Diffusion Theory to Data

Source of data	Reaction	Principal variables	$\frac{(D/\tau)}{(D/\tau)_{\text{standard}}}$	$S_v^2 D_s, \text{sec}^{-1}$
Borgwardt (1970)	$\text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_3$	Particle size	0.11	0.5×10^4
Coutant et al. (1970)	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	Gas composition	0.12	3.5×10^4
	$\text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_3$			

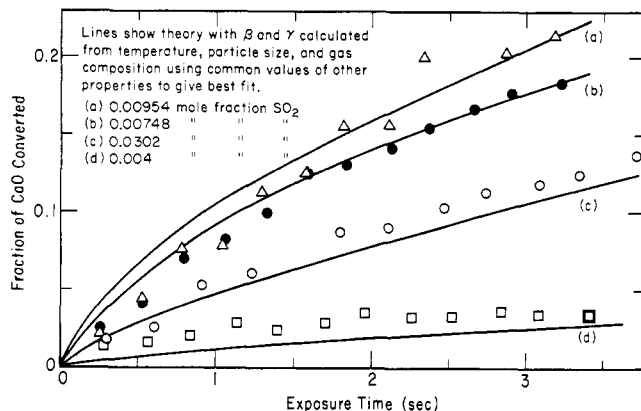


Figure 6. Comparison of diffusion theory with data of Coutant et al. (1970)

Effect of gas composition

and at various temperatures, although at only one value of the particle size, 0.009 cm. When the observed values of the fractional conversion of CaO are plotted logarithmically against times, as in Figure 4, it is once again possible to draw straight lines through the data, which extend from $t = 0.25$ to 3.2 sec. According to Equations 13 and 14, the logarithmic slope should vary from 0.75 if pore diffusion is limiting to 0.50, if the surface reaction rate is limiting. Figure 5 shows a plot of the values of dF/dt against the gas mole fraction. The straight line through the data has a slope of 0.64, nearly half way between the possible extremes expected, indicating that, at least at the intermediate concentrations, the data are in a transition region between limiting pore diffusion and uniform surface rate.

Values of β and γ derived from the Coutant data are listed in Table III, which shows that β is nearly proportional to γ as expected from the theory. One exception is the point at the smallest value of γ , at which the determination of β is least accurate. If the average value of β/γ is used, as before, to find an apparent value of $S_v^2 D_s$, assuming $\alpha = 1/2$ and $\tau = 1$, the result is 190 sec^{-1} .

Once again, as with the previously considered data, it is statistically possible to improve the quality of the comparison between theory and data concerning gas composition by choosing a value of (β/γ) equal to about 0.1 times the "nominal value." The result is that the values of β are reduced below those listed in Table III and the time dependence of the observed conversion is matched much better. When the apparent value of $S_v^2 D_s$ is computed from the results of the nonlinear least-squares procedure, one obtains $S_v^2 D_s \sim 3 \times 10^4 \text{ sec}^{-1}$, which is substantially greater than the apparent value obtained from the Borgwardt data. Table IV summarizes the values found from fitting the two sets of data. Note that the data of Coutant et al. were obtained in an experiment in which limestone particles were injected into the hot gas containing SO_2 , whereas Borgwardt used limestone that had already been calcined to CaO. Thus, in the experi-

ments which lead to the larger apparent value of $S_v^2 D_s$, CO_2 evolution occurred simultaneously with SO_2 absorption.

Figure 6 shows a comparison of the measured values of the fraction of CaO converted vs. time, based on the data of Coutant et al. at 1700°F and $2R = 0.009 \text{ cm}$, and theoretical lines based on the diffusion theory. The two parameters, β and γ , were adjusted to obtain the best fit of the data while maintaining the dependence of these quantities on particle size and gas concentration computed in the theory. The parameters used corresponded to (β/γ) equal to 0.12 times its nominal value and $\beta/\gamma = 11 \text{ sec}^{-1}$. The smaller value of (β/γ) can easily be accounted for by a pore diffusion coefficient smaller than the bulk gas value and tortuosity in the diffusion channels. One sees from the figure that the theory is capable of accounting for effects of composition and time on the conversion in these experiments.

Effect of Temperature on Reaction Rate

The effect of temperature on the reaction rate and on the apparent rate constants is confusing, as shown by the data listed in Table III. At $t < 1845^\circ\text{F}$, the apparent effect corresponds to an activation energy of β^{-1} of about 28 kcal/g-mol. From the definition of β , this quantity is equal to

$$E_{Ds} - 2E_{Dg} + 2RT^2(d \ln S_v/dT)$$

where E_{Ds} and E_{Dg} represent the activation energies for the solid-phase and the gas-phase diffusion coefficients, respectively. [In the range where $\beta t > 1$, the rate of reaction is proportional to $D\beta^{-1/2}$ and its activation energy becomes $1/2 E_{Ds} + RT^2(d \ln S_v/dT)$.] Since E_{Dg} is about 0.8 kcal/g-mol, it follows, if S_v is constant, that $E_{Ds} \sim 30 \text{ kcal/g-mol}$, a value that is too great for comfort. It can hardly represent the activation energy of a true solid-state diffusivity.

A possible explanation is that the porosity of the solid product which forms internally is greater at the higher temperatures in this low range or that S_v is also greater. When we recall that the internal surface area is partly the result of the release of CO_2 inside the porous particles, this assumption may not be unreasonable.

Borgwardt (1970) concluded that the activation energy for his observed chemical "reaction rate constants" was within the range 8–18 kcal/g-mol, depending on the type of natural limestone used to make his calcium oxide particles. The corresponding value for the lower temperatures in Table IV is about 15 kcal/g-mol, which is in qualitative agreement.

Above 1845°F the reaction rate reaches a maximum and the apparent activation of β^{-1} becomes negative. This is probably owing to the sintering of the internal surface so that $d \ln S_v/dT$ becomes negative and offsets E_{Ds} .

Conclusions

The good qualitative agreement of the theory with data expressing the effects of particle size and gas concentration and the rough agreement of apparent values of physical constants with accepted ranges indicate that the pore-diffusion theory is capable of accounting for the main features of the

reaction of gaseous SO₂ with porous limestone particles. The theory is not exact, however, and ought not to be used as a substitute for experiment. It can be used for estimates of the effects of changes in particle size, gas composition, and temperature in a narrow range on the rate of absorption of SO₂ for adjustment of experimental data.

Alternate theories doubtless can be used to fit scattered experimental data such as those referred to here, but the theory proposed here has fewer arbitrary constants than others and appears more rational. With the theory available, costly experimentation may be reduced, if not eliminated, and data taken under idealized laboratory conditions possibly can be applied to the design of practical recovery systems.

APPENDIX

Solution of Differential Equation for Diffusion and Reaction

We wish to find the solution of the problem

$$\frac{1}{\xi^2} \frac{\partial}{\partial \xi} \xi^2 \frac{\partial c}{\partial \xi} = \frac{c}{\left(\int_0^\theta c(\xi, p) dp \right)^{1/2}} \quad (\text{A-1})$$

with the boundary conditions

$$c(\xi, 0) = 0, c(1, \theta) = 1, c_\xi(0, \theta) = 0 \quad (\text{A-2, a, b, c})$$

If we let

$$u^2(\xi, \theta) = \xi \int_0^\theta c(\xi, p) dp \quad (\text{A-3})$$

we find that Equation A-1 becomes the third-order equation

$$\frac{\partial}{\partial \theta} \left(\frac{\partial^2 u^2}{\partial \xi^2} - 2 \xi^{1/2} u \right) = 0 \quad (\text{A-4})$$

(Note that $\xi^{1/2} u(\xi, \theta)$ is proportional to the thickness of the product layer, X .) Integrating Equation A-4 with respect to time gives us

$$\frac{\partial^2 u^2}{\partial \xi^2} - 2 \xi^{1/2} u = G(\xi) \quad (\text{A-5})$$

in which $G(\xi)$ is an arbitrary function of ξ . It can be found from the initial condition. Since $u(\xi, 0)$ and $u_{\xi\xi}(\xi, 0)$ are both zero, and since Equation (A-5) must apply at $\theta = 0$ as well as at other values of θ , $G(\xi)$ must be zero. Let

$$u^2(\xi, \theta) = \theta F^2(\xi, \theta)$$

so that

$$F(\xi, \theta) = (\xi/\theta) \left(\int_0^\theta c(\xi, p) dp \right)^{1/2}$$

(Note that this relationship makes $F(0, \theta) = 0$.) The problem is now reduced to

$$\frac{\partial^2 F}{\partial \xi^2} - 2 (\xi/\theta)^{1/2} F^{1/2} = 0; F(0, \theta) = 0; F(1, \theta) = 1 \quad (\text{A-6})$$

A numerical solution is possible as follows:

Obviously F depends on both ξ and θ , but one can start the integration of Equation A-6 in the ξ -direction to obtain F vs. ξ at fixed θ . The integration begins at $\xi = 0$, where $F = 0$, regardless of θ , and continues to $\xi = 1$ where $F = 1$, regardless of θ . At intermediate points, F depends on θ . To begin the integration, one must supply a value of $\partial F / \partial \xi(0, \theta)$, say $b(\theta)$. The correct value of c is the one that yields $F(1, \theta) = 1$. Near $\xi = 0$, $F = \xi b(\theta)$ and

$$b(\theta) = \frac{1}{\theta} \int_0^\theta c(0, p) dp \quad (\text{A-7})$$

from which the concentration of the gaseous reagent at the center of the porous sphere can be found:

$$c(0, \theta) = \frac{d}{d\theta} [\theta b(\theta)]$$

The method of Runge-Kutta-Gill was used with a digital computer to obtain the numerical values listed in Table I.

The concentration gradient at the surface, $(\partial c / \partial \xi)(1, \theta)$, referred to as the dimensionless reaction rate in the text, can be found from the numerical solution by means of the equation

$$(\partial c / \partial \xi)(1, \theta) = -1 + (dF^2 / d\xi)(1) \quad (\text{A-8})$$

The dimensionless fractional conversion can be calculated conveniently from

$$\int_0^\theta c_\xi(1, p) dp = 4/3 \int_0^\theta [p^{1/4} c_\xi(1, p)] d(p^{3/4}) \quad (\text{A-9})$$

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Nomenclature

- a = radius of subparticle of solid reagent
- C = concentration of reactant gas inside porous particle, mole/volume; subscript o refers to gas outside porous sphere
- D = diffusion coefficient of gaseous reactant in pores
- D_s = diffusivity of SO₂ through solid product shell
- \mathfrak{F} = dimensionless fraction conversion, equal to γF
- F = fraction conversion of solid reagent in porous particle
- N = rate of absorption of gaseous reagent per unit exterior surface of porous particle
- r = radius in porous particle
- R = radius of porous solid particle
- S_p = surface area for reaction per unit volume of large particle
- t = time following first exposure of porous particle to gas
- T = gas temperature, °K
- v = reaction rate on interior surface of porous particle, mol/(sec)(cm²)
- X = thickness of solid product shell
- y = mole fraction SO₂ in gas outside porous sphere

GREEK LETTERS

- α = fraction by volume of pores in large particle
- β = time constant defined in Equation 7
- γ = combination of physical constants defined in Equation 12, used for expressing the fraction conversion of the solid reagent
- ρ_s = molar concentration of solid reagent, mol/cc
- θ = dimensionless time, equal to βt
- ξ = dimensionless radial distance in porous sphere
- τ = tortuosity of pores

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