Effect of Pressure on Predicted and Observed Diffusion Rates in Constricted Pores—A Theoretical Study

H. W. HAYNES, JR. and L. F. BROWN
University of Colorado, Boulder, Colorado

A problem frequently encountered in heterogeneous catalysis is that of determining the effectiveness of the single catalyst particle. More often than not the reaction rate–particle size relationship is unavailable, and the Thiele modulus must be estimated. This in turn requires the estimation of the effective diffusivity of the reacting molecules within the catalyst pore structure. A number of models of catalyst pore structure have been proposed for the purpose of predicting effective diffusivities (*2, 3, 4, 8, 10*). One of these, the parallel pore model, has achieved wide recognition because of its conceptual simplicity, mathematical tractability, and ability to represent experimental data at least as well as the more sophisticated models.

The parallel pore model may be visualized as a bundle of pores extended completely through the porous medium. It is assumed that the bundle is oriented in the direction of diffusion and that the radius of each pore is uniform across the length of the pellet. The frequency of the occurrence of pores of various sizes is determined by the pore size distribution function. For the problems considered here, the parallel pore model leads to the same computations as the model of Johnson and Stewart (*4*). The simplified form of the model in which all pores are of the same diameter is the same as the model proposed earlier by Wheeler (*10*).

According to convention, a factor is included in the parallel pore model to account for nonidealities in the porous structure. Termed the tortuosity factor, it is defined as the ratio of the flux predicted by the model to the observed flux. As the name implies, one correction included in this factor is for deviousness of the diffusion path. But other nonidealities such as number of intersections, cross-sectional and longitudinal shapes of pores, and pore constrictions are also reflected in the tortuosity factor.

In view of the complicated nature of the tortuosity factor, it is perhaps surprising that the parallel pore model using a tortuosity factor of three* is adequate in most cases for predicting effective diffusivities in commercial catalyst pellets to within a factor of two (*1, 4, 7*). There are notable exceptions, however, one of them being ascribed to severe pore constrictions (*1*). In this instance a tortuosity factor of 30 was required to bring the predicted and observed results into agreement.

An additional, and even more surprising, observation in two of these studies was the essential constancy of the tortuosity factor with varying pressure (*1, 7*). Of the 17 porous materials studied over pressure ranges of 1 to 20 and 1 to 65 atm., only one required a change in tortuosity factor greater than 35% over the pressure range investigated; the increase was about 70% over the range 1 to 65 atm. In all the other systems studied, the tortuosity factor was essentially constant, even when using materials where pore constrictions were believed to be present.

There seems to be no obvious reason why the tortuosity factor should remain constant as the pressure changes. In this communication we investigate theoretically the effect of pressure upon the parallel pore model predictions when pore constrictions are known to be present. If the constancy of the tortuosity factor with pressure can be shown to be an inherent property of the calculations, then the method may be used with some confidence for extrapolation of measurements to new values of the total pressure.

FLOW WITHIN CONSTRICTED PORES

The development is similar in some respects to that of Michaels (*6*). We begin by considering diffusion in a series combination of cylindrical pores of two sizes, r_I and r_{II}, with $r_I \geqq r_{II}$. Each of n identical pore assemblies extends through the porous medium, and m identical cells are repeated within each assembly. This rather extreme idealization of a constricted pore system is illustrated in Figure 1. For purposes of simplification, entrance and exit effects are neglected. The experimental observations reported above were made in a Wicke-Kallenbach apparatus (*11*), so this analysis assumes the appropriate boundary conditions.

The rate of diffusion through this system of pores can be calculated for some limiting situations. If the diffusion mechanism is one of ordinary or bulk diffusion and Fick's Law can be integrated across each pore segment, then

$$F_B = (n\pi r_I^2)\left[\frac{C_T D_{AB}}{\alpha(l_I/m)}\right]\ln\left[\frac{1-\alpha y_{2i}}{1-\alpha y_{2i-1}}\right], \quad i = 1, 2, \ldots m \qquad (1)$$

and

$$F_B = (n\pi r_{II}^2)\left[\frac{C_T D_{AB}}{\alpha(l_{II}/m)}\right]\ln\left[\frac{1-\alpha y_{2i-1}}{1-\alpha y_{2i-2}}\right], \quad i = 1, 2, \ldots m \qquad (2)$$

These equations can be rearranged and combined to give

$$F_B = (n\pi r_I^2)\left(\frac{C_T D_{AB}}{\alpha l_I}\right)\ln\left\{\prod_{i=1}^{m}\left[\frac{1-\alpha y_{2i}}{1-\alpha y_{2i-1}}\right]\right\} \qquad (3)$$

$$F_B = (n\pi r_{II}^2)\left(\frac{C_T D_{AB}}{\alpha l_{II}}\right)\ln\left\{\prod_{i=1}^{m}\left[\frac{1-\alpha y_{2i-1}}{1-\alpha y_{2i-2}}\right]\right\} \qquad (4)$$

Another important relationship may be obtained by cross-multiplying the two terms in brackets in the previous two equations and taking logarithms of the product

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H. W. Haynes, Jr., is now with Esso Research and Engineering Co., Baytown, Texas.

* As pointed out in reference *4*, the theoretical correction for deviousness in a three-dimensional, isotropic medium is three.

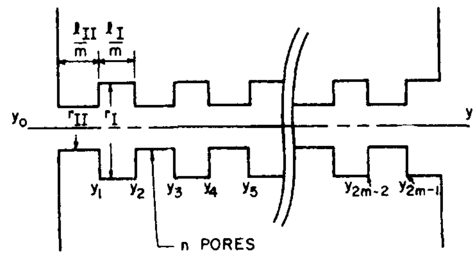

Fig. 1. Model of constricted pore system.

$$\ln\left[\frac{1-\alpha y_{2m}}{1-\alpha y_0}\right] = \ln\left\{\prod_{i=1}^{m}\left[\frac{1-\alpha y_{2i}}{1-\alpha y_{2i-1}}\right]\right\} + \ln\left\{\prod_{i=1}^{m}\left[\frac{1-\alpha y_{2i-1}}{1-\alpha y_{2i-2}}\right]\right\} \qquad (5)$$

Substituting from Equations (3) and (4) for the terms on the right and solving for F_B

$$F_B = \left[\frac{R^2(L+1)}{R^2+L}\right](n\pi r_{II}^2)\left[\frac{C_T D_{AB}}{\alpha(l_I+l_{II})}\right]\ln\left[\frac{1-\alpha y_{2m}}{1-\alpha y_0}\right] \qquad (6)$$

in which

$$R = \frac{r_I}{r_{II}} \qquad L = \frac{l_I}{l_{II}} \qquad (7)$$

In a similar manner, the Knudsen diffusion equation can be applied to the system with the following result:

$$F_K = \left[\frac{R^3(L+1)}{R^3+L}\right]\left[(n\pi r_{II}^2)(C_T\, D_{KII})\left(\frac{y_0-y_{2m}}{l_I+l_{II}}\right)\right] \qquad (8)$$

At very low pressures where the mean free path of the diffusing molecules is large relative to the radius of the larger pores, the molar diffusion through the system of pores is given by Equation (8). At very high pressures the mean free path is small relative to the pore sizes, molecule-wall collisions become unimportant, and Equation (6) applies.

PARALLEL PORE MODEL PREDICTIONS

Use of the True Pore Size Distribution

The diffusion rates given by Equations (6) and (8) may be compared with the rates predicted by the parallel pore model in the ordinary and Knudsen diffusion regions, respectively. The tortuosity factors (or more properly the "constriction factors" because we choose to eliminate from consideration all other nonidealities) can thus be evaluated at the extreme limits in pressure where these transport mechanisms predominate. The parallel pore model regards the porous medium as composed of n_I' pores of radius r_I in parallel with n_{II}' pores of radius r_{II}, and therefore

$$\frac{n_I'}{n} = \frac{\pi r_I^2\, l_I}{\pi r_I^2(l_I+l_{II})} = \frac{L}{L+1} \qquad (9)$$

$$\frac{n_{II}'}{n} = \frac{\pi r_{II}^2\, l_{II}}{\pi r_{II}^2(l_I+l_{II})} = \frac{1}{L+1} \qquad (10)$$

The total predicted diffusion rate is obtained by summing each individual pore contribution. In the ordinary diffusion region

$$F_B' = (n_I'\,\pi r_I^2)\left[\frac{C_T D_{AB}}{\alpha(l_I+l_{II})}\right]\ln\left[\frac{1-\alpha y_{2m}}{1-\alpha y_0}\right] + (n_{II}'\,\pi r_{II}^2)\left[\frac{C_T D_{AB}}{\alpha(l_I+l_{II})}\right]\ln\left[\frac{1-\alpha y_{2m}}{1-\alpha y_0}\right] \qquad (11)$$

Or, after substituting for n_I' and n_{II}' from Equations (9) and (10)

$$F_B' = \left(\frac{LR^2+1}{L+1}\right)(n\pi r_{II}^2)\left[\frac{C_T D_{AB}}{\alpha(l_I+l_{II})}\right]\ln\left[\frac{1-\alpha y_{2m}}{1-\alpha y_0}\right] \qquad (12)$$

According to definition, the constriction factor is equal to the ratio of diffusion rates given by Equations (12) and (6). Thus

$$\gamma_B' = \frac{F_B'}{F_B} = \frac{(L+R^2)(LR^2+1)}{R^2\,(L+1)^2} \qquad (13)$$

And in an analogous manner it can be shown that when Knudsen diffusion predominates:

$$F_K' = \left(\frac{LR^3+1}{L+1}\right)\left[(n\pi r_{II}^2)(C_T D_{KII})\left(\frac{y_0-y_{2m}}{l_I+l_{II}}\right)\right] \qquad (14)$$

$$\gamma_K' = \frac{F_K'}{F_K} = \frac{(L+R^3)(LR^3+1)}{R^3\,(L+1)^2} \qquad (15)$$

The values of the constriction factor for both Knudsen flow and bulk diffusion are thus expressible in terms of only the ratios R and L. Since R is always greater than or equal to unity, the forms of the expressions require that the constriction factors be greater than or equal to unity. Thus, under these circumstances, the presence of constrictions gives a flux lower than predicted, which is not surprising.

Some numerical values of the constriction factors are presented in the third and fourth columns of Table 1 for a range of L and R. It shows that drastic changes in the constriction factor, and hence in the tortuosity factor, are possible with changing pressure. This table indicates that if the parallel pore model were used for extrapolating measurements with pressure in a severely constricted pore system, and the controlling mechanism changed from Knudsen to bulk diffusion (or vice versa), the tortuosity factor should change by a factor of perhaps 5 or 6. Furthermore, as the constriction factor for Knudsen flow is greater than the constriction factor for bulk diffusion, somewhere during the change from Knudsen to bulk diffusion the tortuosity factor for the constricted pore system should decrease. These two behavior patterns are completely contrary to the experimental observations discussed earlier.

Use of the Apparent Pore Size Distribution

The answer to the riddle may very possibly lie in the nature of the techniques for obtaining pore distributions. Any errors or invalid assumptions in the pore-size distribution determination would be reflected in the model predictions and therefore in the tortuosity factor. The distributions are obtained by mercury penetration and nitrogen sorption methods. If a constricted pore system is analyzed by mercury penetration, the volumes of the constricted pores are regarded as being composed of pores whose size is the same as the necks of the constrictions (9). The same is true of a pore-size distribution obtained from the nitrogen desorption isotherm if the theory of McBain (5) explaining sorption hysteresis is accepted. It therefore appears from the apparent pore-size distribution that the porous medium is composed of n'' pores of radius r_{II}. The relationship between the real and the apparent pore structures is

$$\frac{n''}{n} = \frac{\pi r_I^2 \, l_I + \pi r_{II}^2 \, l_{II}}{\pi r_{II}^2 \, (l_I + l_{II})} = \frac{R^2L + 1}{L + 1} \tag{16}$$

In the bulk diffusion region, the molar diffusion rate predicted by the model using the apparent pore size distribution is

$$F_B'' = (n''\pi r_{II}^2) \left[\frac{C_T D_{AB}}{\alpha(l_I + l_{II})} \right] \ln \left[\frac{1 - \alpha y_{2m}}{1 - \alpha y_0} \right] \tag{17}$$

or

$$F_B'' = \left(\frac{R^2L + 1}{L + 1} \right) (n\pi r_{II}^2) \left[\frac{C_T D_{AB}}{\alpha(l_I + l_{II})} \right] \ln \left[\frac{1 - \alpha y_{2m}}{1 - \alpha y_0} \right] \tag{18}$$

Combining with Equation (6)

$$\gamma_B'' = \frac{F_B''}{F_B} = \frac{(R^2L + 1)(R^2 + L)}{(L + 1)^2 R^2} \tag{19}$$

In the Knudsen diffusion region it can be similarly shown that

$$F_K'' = \left(\frac{R^2L + 1}{L + 1} \right) \left[(n\pi r_{II}^2)(C_T D_{KII}) \left(\frac{y_0 - y_{2m}}{l_I + l_{II}} \right) \right] \tag{20}$$

$$\gamma_K'' = \frac{F_K''}{F_K} = \frac{(R^2L + 1)(R^3 + L)}{(L + 1)^2 R^3} \tag{21}$$

It might be surmised that the Knudsen and bulk diffusion situations would reflect the limiting values of the constriction factor. One of the authors (3) has shown, by some rather involved algebra, that this is rigorously true given the underlying assumptions used here. From Equations (19) and (21) therefore

$$\frac{(R^2L + 1)(R^3 + L)}{(L + 1)^2 R^3} \leq \gamma'' \leq \frac{(R^2L + 1)(R^2 + L)}{(L + 1)^2 R^2} \tag{22}$$

TABLE 1. EFFECT OF PORE CONSTRICTIONS ON CONSTRICTION FACTORS USING THE PARALLEL PORE MODEL

L	R	γ_K'	γ_B'	γ_K''	γ_B''
0.1	1.0	1.0	1.0	1.0	1.0
0.1	2.0	1.51	1.19	1.17	1.19
0.1	5.0	11.2	2.90	2.90	2.90
0.1	10.0	83.4	9.09	9.09	9.09
1.0	1.0	1.0	1.0	1.0	1.0
1.0	2.0	2.53	1.56	1.41	1.56
1.0	5.0	31.8	6.75	6.54	6.75
1.0	10.0	250.0	25.5	25.2	25.5
10.0	1.0	1.0	1.0	1.0	1.0
10.0	2.0	1.51	1.19	0.76	1.19
10.0	5.0	11.2	2.90	2.24	2.90
10.0	10.0	83.4	9.09	8.33	9.09

According to this expression, the presence of pore constrictions can lead to predicted fluxes greater than or less than the observed fluxes, depending upon the magnitude of the quantities R and L. For L less than unity, the predicted flux is greater than the observed flux for practically all R, but it is interesting that pore constrictions can apparently lead to predicted fluxes less than the observed for large L and relatively small R at pressures where bulk diffusion is not completely controlling. [The upper limit of Equation (22) which is also the bulk diffusion limit can never be less than unity.] In these cases, the constriction factor can be expected to increase slightly as pressure is increased and the diffusion mechanism changes from predominately Knudsen diffusion to predominately bulk diffusion.

Perhaps the most important deduction from Equation (22), however, is that the constriction factor remains essentially constant and independent of pressure for most values of L and R. The fifth and sixth columns of Table 1 illustrate this point. For a large number of L and R combinations, the effect of pore constrictions is completely consistent with the experimental observation that the tortuosity factor does not vary greatly with pressure. At the same time the constriction factor, and thus the tortuosity factor, might be extremely large.

It may be added that since the essential constancy of the constriction factor exists for any single cylindrical pore of arbitrary dimensions, constricted or not, it would also exist for a summation of pores distributed over any range of pore sizes. Therefore, if the parallel pore model is used, the constriction factor of any material whose pores are reasonably simulated by the present model should remain unaffected by pressure.

CONCLUSIONS

Using a rather crude idealization of a constricted pore system, the behavior of diffusion rates with changing pressure within some porous systems has been satisfactorily explained. According to this analysis, the simultaneous effect of pore constrictions on both pore distribution determination and the parallel pore model prediction will result in a tortuosity factor essentially independent of pressure. At the same time the predicted rates may be higher or lower than the observed rates.

Moreover, the analysis also suggests that the usage of a true pore-size distribution, if one can be obtained, will always lead to tortuosity factors greater than or equal to three. In this case, the tortuosity factor would also be expected to decrease as pressure increases and the diffusion mechanism changes from predominantly Knudsen diffusion to predominantly bulk diffusion.

Since factors other than pore constrictions can affect the tortuosity factor, this communication has shown only that a necessary condition for the essential constancy of the tortuosity factor is usually fulfilled when the parallel pore model is used in conjunction with the apparent pore size distribution. So, although extrapolation of diffusion data with pressure may be made with some confidence for materials whose porous structure is reasonably represented by the present model, the possibility of occasional exceptions should always be remembered.

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NOTATION

C_T = total concentration, gm.-moles/cc.
D_{AB} = bulk diffusivity of substance A in substance B, sq.cm./sec.
D_K = Knudsen diffusivity of substance A, sq.cm./sec.
F = molar diffusion rate of substance A, gm.-moles/sec.
l = total of length of given size subpore within a single pore assembly, cm.
L = l_I/l_{II}, dimensionless
m = number of cells in a single pore assembly, dimensionless
n = number of pore assemblies within the porous pellet, dimensionless
r = radius of pore, cm.
R = r_I/r_{II}, dimensionless
y = mole fraction of substance A, dimensionless
α = 1 + (ratio of molar rates of diffusing substances), dimensionless
γ = constriction factor—contribution of pore constrictions to tortuosity factor, dimensionless
I = property of pore of radius r_I
II = property of pore of radius r_{II}
B = bulk diffusion completely controlling
K = Knudsen flow completely controlling
$''$ = predicted in situation where present method of obtaining pore-size distributions is used
$'$ = predicted in situation where true pore-size distribution is used

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Bimodal Wave Formation on Thin Liquid Films Flowing down a Plane

WILLIAM B. KRANTZ
University of Colorado, Boulder, Colorado

and SIMON L. GOREN
University of California, Berkeley, California

In a recent paper Krantz and Goren (*8*) presented the first measurements of wave lengths, wave velocities, and amplification rates of waves on thin liquid films flowing down an inclined plane, resulting from imposed disturbances of controlled amplitude and frequency. In a second paper the authors (*9*) presented measurements of equilibrium wave amplitudes for viscous oils and compared these data to a new theory describing finite-amplitude, two-dimensional, equilibrium waves on thin films flowing down an inclined plane.

This note describes the formation of "bimodal waves" on thin liquid films flowing down an inclined plane. A "bimodal wave" consists of a fundamental wave and a second superimposed distinct wave having the first harmonic frequency of the fundamental wave. In general these component waves of the bimodal wave have different wave velocities and amplification rates and thus are observed to pass each other and change form as they travel down the column. Such waves also were reported by Tailby and Portalski (*12*), Jones (*5*), and Hallett (*4*) in their studies of thin liquid films subject to room disturbances. It is important to note that bimodal waves do not imply a Fourier decomposition of a nonsinusoidal wave form. Bimodal waves refer to two distinct wave forms traveling down the column with distinct wave velocities.

LINEAR STABILITY THEORY

Attempts to describe the formation and growth of waves on thin liquid films can be broadly classified into linear and nonlinear stability theories (*7* to *9*). Investigations into the theory of linear stability are based on the assumption that infinitesimally small disturbances are superimposed on the laminar film flow. The theory has been developed in an effort to understand the mechanism and conditions necessary for transition away from unrippled laminar film flow and, as such, can predict only exponential growth or decay of infinitesimal disturbances.

The next step in the understanding of the transition away from unrippled laminar film flow is the consideration of disturbances which have grown too large to be governed by a theory of infinitesimal disturbances. In order to predict the behavior of these larger amplitude disturbances and to understand the physical processes which must occur to slow down the exponential growth it is necessary to consider the nonlinear terms in the equations of motion.

One conclusion which can be drawn from the linear stability theory of thin films flowing down a plane is that the flow becomes unstable at very small Reynolds numbers; vertical film flow is always unstable. Hence, at these small Reynolds numbers viscous forces are of comparable magnitude to gravity and inertia forces. Very few theories of finite amplitude waves have appeared which consider viscous effects based on rigorous hydrodynamics.

NONLINEAR STABILITY THEORY

With the exception of the equilibrium wave amplitude correlation developed by Krantz and Goren (*9*), all the nonlinear theories, which include both viscous terms and surface tension (*1*, *3*, *6*, *10*, *11*), consider only small amplitude waves. These theories thus are restricted to