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The Prediction of Diffusion Rates in Porous Materials at Different Pressures

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Two current models for diffusion in porous catalysts are applied to diffusion data obtained over the pressure range 1–20 atm, using 12 porous materials with widely different pore-size distributions.

The results of this study confirm a previous study of Satterfield and Cadle in two respects—a model of a porous structure by Johnson and Stewart can be used to predict diffusion rates to within a factor of 2 with occasional exceptions, and this model is good for extrapolating data obtained at one pressure to another pressure. In addition, the present investigation found little choice between the absolute predictive capabilities of the Johnson and Stewart model and one of Wakao and Smith, although the latter is inadequate for extrapolation with pressure. Evidence indicates that the infrequent, though serious, exceptions may be the result of severe pore constrictions. A possible converging trend of the value of (observed flux/predicted flux) when using the Wakao and Smith model at higher pressures is also observed and discussed.

INTRODUCTION

The importance of intraparticle diffusion to heterogeneous catalysis and adsorption has been recognized for many years, and its significance is attested by the many articles and reviews treating diffusion in porous media. The result has been a steady increase in understanding in this area, coupled with a concomitant increase in the ability to predict diffusion rates in porous catalysts and adsorbents from simple measurements.

At the present time, two models containing no undetermined parameters appear to be popular for the prediction of diffusion rates in both unimodal and bimodal porous materials. A model developed by Johnson and Stewart (*1*) utilizes the concept of randomly oriented continuous circular pores piercing the solid; a model developed by Wakao and Smith (*2*) has noncontinuous circular pores occurring randomly throughout the solid. Both of these models employ the pore-size distribution obtained from mercury porosimeter and adsorption–desorption measurements, and are independent of diffusion measurements. A third model has recently been proposed (*3*) but has not yet attained the popularity of the first two.

In a recent extensive study of diffusion in bimodal porous catalysts, Satterfield and Cadle (*4, 5*) concluded that with sporadic exceptions, the Johnson and Stewart model could be used to predict diffusion rates in these materials within a factor of 2. No method of predicting the exceptions (2 of the 17 catalysts studied) was offered, however, except to note that both of them had been calcined at high temperatures. Since one of the exceptions was incorrect by a factor of approximately 20, this may represent a significant flaw in the predictive ability of this model.

For the 15 well-behaved materials, it was concluded that the Johnson and Stewart model was superior to the Wakao and Smith model. For extrapolating diffusion measurements from one pressure to another, the Johnson and Stewart model appeared to be completely satisfactory for the five materials tested over a range of 1–65 atm, while the Wakao and Smith model was inadequate in this respect.

Data concerning diffusion through porous materials are infrequent in the technical literature, and as predictive models are improved, there is a need for additional testing and study. This paper reports some additional results of comparing the predictive capabilities of the Johnson and Stewart and the Wakao and Smith models for 12 porous materials covering a wide variety of pore characteristics. Diffusion measurements were made over a range of 1–20 atm pressure, and the results compared with those predicted by the two models. Thus the scope of this paper is similar to that of the Satterfield-Cadle articles, though materials containing a somewhat wider variety of pore characteristics were tested at elevated pressures.

For the materials reported here, there appears to be little choice between the absolute predictive capabilities of the Johnson and Stewart and the Wakao and Smith models. In addition, two of the conclusions of the Satterfield-Cadle articles are confirmed: the approximate factor of 2 for the predictive ability of the Johnson and Stewart model, again with an occasional exception; and the superior capability of the Johnson and Stewart model in extrapolating data from one pressure to another.

NOMENCLATURE

p	Pressure (atm)
r_a	Volume-averaged macropore radius (Å)
r_i	Volume-averaged micropore radius (Å)
S_{BET}	BET surface area (m^2/g)
S_{cum}	Total cumulative surface area from pore-size distribution (m^2/g)
V_a	Cumulative macropore volume from pore-size distribution (cc/g)
V_{app}	Apparent volume of catalyst pellet (cc/g)
V_i	Cumulative micropore volume from pore-size distribution (cc/g)
V_p	Total pore volume from pore-size distribution (cc/g)
$(V_p)_{He}$	Total pore volume from helium displacement measurements (cc/g)
Θ_a	Macropore void fraction (dimensionless)
Θ_i	Micropore void fraction (dimensionless)

EXPERIMENTAL PROGRAM

The data which are reported in this paper result from two different experimental investigations (*6*, *7*). Three of the samples (Nos. 10, 11, and 12) were tested in the earlier study, and the other nine in the later one. A brief description of the materials studied is presented in Table 1, and their properties are tabulated in Tables 2 and 3. The complete pore-size distributions are presented in refs. (*6*) and (*7*).

In these studies, pellets of each material were chosen at random and machined to cylinders of $\frac{3}{8}$, $\frac{1}{4}$, or $\frac{3}{16}$ inch diameter by $\frac{3}{16}$ inch thick. The pellets were first used in a series of Wicke-Kallenbach experiments for determining the transport through the porous materials as a function of pressure. Helium and nitrogen were the diffusing gases with the helium flux being the one reported. The helium is reported because the theory behind the models is based upon gas-phase diffusion, and it was desired to eliminate the possibility of surface diffusion insofar as possible.

The Wicke-Kallenbach experiment has been widely used and thoroughly described many times [e.g., ref. (*8*)], and the particular details of the apparatus and procedure used in these studies are available in refs. (*6*) and (*7*), together with the diffusion data obtained. The principal experimental difference between the two investigations was the use of three pellets mounted in parallel in the earlier study as opposed to the use of a single pellet in the later one. The lower pressure data obtained in the earlier study are open to some question, and are not reported here. Using samples of porous material No. 1, the agreement between the two studies over the higher range reported here was good, the differ-

TABLE 1

MANUFACTURER'S DESCRIPTION OF MATERIALS INVESTIGATED

Sample No.	Description
1	Harshaw AL-1404T Alumina Catalyst ($\frac{3}{8} \times \frac{3}{8}$ inch tablets). A tableted alumina containing 96% Al_2O_3. Used as a catalyst support, drying agent, and for dehydration reactions.
2	Girdler G-3B Chromium Promoted Iron Oxide Catalyst ($\frac{3}{8} \times \frac{3}{8}$ inch tablets). Primarily used as a water-gas shift catalyst.
3	Girdler G-35 Cobalt Molybdenum on Alumina ($\frac{3}{16} \times \frac{3}{16}$ inch tablets). A cobalt-molybdenum catalyst supported on alumina used as a hydrodesulfurization catalyst.
4	Catalysts and Chemicals C-46-2 Nickel Hydrogenation Catalyst ($\frac{3}{16} \times \frac{3}{16}$ inch tablets). Nickel oxide on an active support with hydraulic binder, for hydrogenation of aldehydes, ketones, and benzene, and for special methanation applications.
5	Girdler G-56B Nickel Reforming Catalyst ($\frac{1}{2}$ inch cylinders). A nickel base catalyst for reforming of lower molecular weight hydrocarbons with steam, carbon dioxide, or steam and air at temperatures above 110°F.
6	Girdler T-126 Activated γ-Alumina ($\frac{1}{4} \times \frac{1}{4}$ inch tablets). Primarily used as a catalyst support.
7	Harshaw ZN-0103 Zinc Catalyst ($\frac{1}{4} \times \frac{1}{4}$ inch tablets). A desulfurization catalyst containing 75% ZnO, alumina, magnesia, calcium oxide, and chromium oxide.
8	Corning Porous Glass Code 7930 ($\frac{3}{16}$ inch sheets). An intermediate material obtained after leaching but before firing in the manufacture of Vycor brand 96% silica glassware.
9	Catalysts and Chemicals C-20-6A Cobalt Molybdenum Catalyst ($\frac{3}{16} \times \frac{3}{16}$ tablets). Cobalt oxide and molybdenum oxide on low-sodium activated alumina support. Used in the hydrotreating of petroleum feedstocks by hydrogenation, hydrogenolysis, desulfurization, and denitrification.
10	Harshaw AL-0104T Alumina Catalyst ($\frac{1}{4} \times \frac{1}{4}$ inch tablets). A tableted activated alumina containing 99% Al_2O_3. Used commercially as a catalyst support, drying agent, and for dehydration purposes.
11	Kaiser KA-101 Active Alumina ($\frac{1}{4}$–$\frac{1}{2}$ inch balls). An adsorbent form of alumina produced by processing alumina trihydrate. Used as a desiccant or catalyst carrier.
12	Alcoa F-3 Activated Alumina (1–2 inch granules). An activated alumina manufactured by thermally treating granules of hydrated alumina. Used principally as a desiccant.

TABLE 2

PHYSICAL PROPERTIES OF MATERIALS INVESTIGATED

Sample No.	V_{app} (cc/g)	V_a (cc/g)	V_i (cc/g)	V_p (cc/g)	$(V_p)_{He}$ (cc/g)	S_{BET} (m²/g)	Θ_a	Θ_i	Micropore limit[a] (Å)	r_a (Å)	r_i (Å)
1	0.763	0.0815	0.376	0.458	0.472	195	0.107	0.493	260	9878	39.9
2	0.544	0.339	0.000	0.339	0.366	30	0.623	0.000	39.8	330	0.0
3	0.604	0.0790	0.246	0.325	0.321	237	0.131	0.408	148	4233	23.9
4	0.598	0.170	0.141	0.311	0.319	93	0.284	0.236	78.0	1147	28.3
5	0.562	0.184	0.0445	0.229	0.229	15	0.328	0.0792	97.0	993	33.5
6	0.790	0.156	0.344	0.500	0.499	210	0.198	0.435	140	3758	33.2
7	0.367	0.117	0.0171	0.134	0.153	15	0.318	0.0466	84.0	797	35.0
8	0.693	0.000	0.226	0.226	—	106	0.000	0.326	23500	0	55.4
9	0.766	0.0860	0.363	0.449	0.477	202	0.112	0.474	143	725	42.2
10	0.666	0.0710	0.310	0.381	0.386	78	0.107	0.465	1400	19460	137.0
11	0.775	0.104	0.372	0.476	0.477	256	0.135	0.479	340	21050	33.6
12	0.591	0.166	0.0746	0.241	0.249	36[b]	0.282	0.126	120	6988	32.3

[a] The point of minimum slope in the cumulative volume-pore radius curve. All pores below this point are regarded as belonging to the micropore system, and all pores above are regarded as belonging to the macropore system. This value significantly affects the results of the Wakao and Smith model.

[b] Alcoa reports that their F-3 alumina possesses surface areas of 150-185 m²/gm. There is no explanation of this disparity.

TABLE 3
Percentages of Pore Volumes within Different Size Ranges

Sample No.	Range of pore radii (Å)				
	<100	100–1000	1000–5000	5000–10 000	>10 000
1	80.1	5.0	10.8	2.8	1.2
2	2.2	97.0	0.5	0.1	0.3
3	74.5	8.9	10.4	5.5	0.6
4	46.6	37.8	14.3	0.8	0.5
5	19.4	70.1	8.0	0.9	1.6
6	67.2	12.8	12.4	6.4	1.1
7	13.0	80.2	4.8	0.7	1.2
8	98.1	1.6	0.2	0.1	—
9	74.6	23.6	1.2	0.2	0.3
10	61.1	18.2	13.0	5.3	2.4
11	73.6	7.2	7.0	2.7	9.5
12	30.0	30.8	35.8	1.3	2.1

ences never exceeding 10% of the observed readings.

For each material, either the one pellet or one of the pellets used in the Wicke-Kallenbach experiment was then used for the determination of the pore-size distribution. Nitrogen adsorption and desorption isotherms were determined on a Numinco-Orr nitrogen adsorption apparatus, and mercury penetration measurements were carried out on an Aminco Model 5-7119, 15 000 psi porosimeter. A value of 885 000 (psia) (Å) was assumed for the product $(p)(r)$ in the calculation of the mercury penetration results. The nitrogen desorption isotherm was used for determining the pore-size distribution, using the method of Barrett, Joyner, and Halenda (*9*). The mercury penetration and nitrogen sorption results were joined at the arbitrary pore radius of 100 Å.

Results and Discussion

The results consist of the application of the models of Johnson and Stewart and of Wakao and Smith to the diffusion data obtained. The results are plotted in the form of the ratio (observed He flux)/(predicted He flux) as a function of total pressure. These plots are presented in Fig. 1 for the Johnson and Stewart model and in Fig. 2 for the Wakao and Smith model.

Two conclusions are immediately apparent. Within the pressure range covered, there is little to choose between the two models as far as absolute accuracy is concerned, since over the pressure range studied both models predict the diffusion rates for 11 of the 12 materials within the factor of 2 [0.5 < (observed/predicted) < 2.0] observed by Satterfield and Cadle. But for extrapolation with pressure, the Johnson and Stewart model shows unquestioned superiority. It also appears from Fig. 1 that the tortuosity factor of 3 used by Johnson and Stewart gives predictions in better agreement with our experimental

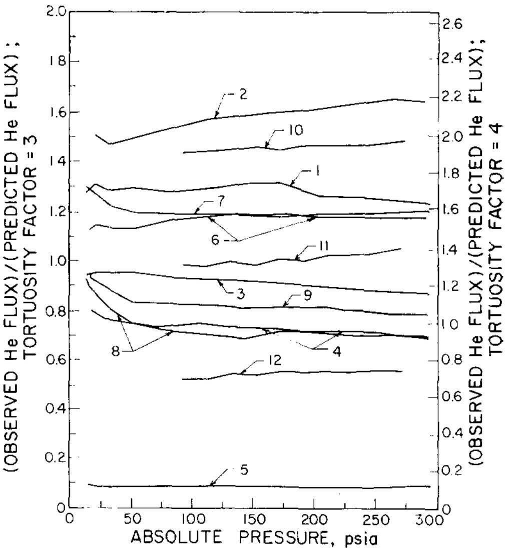

Fig. 1. Predictive capability of Johnson and Stewart model.

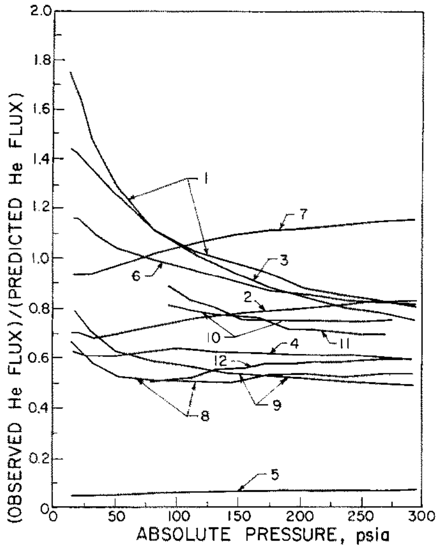

FIG. 2. Predictive capability of Wakao and Smith model.

results than the tortuosity factor of 4 recommended by Satterfield and Cadle (*4*).

Two of the catalyst types used in the present study were also in the group tested by Satterfield and Cadle (*4*). For the T-126, at atmospheric pressure, they reported a tortuosity factor of 3.6 as compared with 2.7 observed in the present study; the respective values for the G-35 were 4.9 and 3.2. The relatively minor differences between the pore-size distributions of Cadle (*10*) and of the present work for the same catalyst types would tend to cause deviations in the direction opposite to that observed if diffusion measurements were identical; thus the cause of the different tortuosity factors appears to lie in the measured transport values. However, manufacturers do emphasize that there may be variations among different batches of the same material (*4*), and this may be the root cause of the different tortuosity factors.

One of the 12 materials studied—the G-56B catalyst—was clearly exceptional. Neither the Johnson and Stewart nor the Wakao and Smith model was adequate for predicting the diffusion rates within this catalyst to anything approaching a desirable engineering accuracy. Similar problems were noted by Satterfield and Cadle with 2 of the 17 materials that they studied.

Often unexpectedly low diffusion rates are attributed to dead-end pore effects. These cannot be excluded, but a second possible explanation which is consistent with the properties of the pore-size distribution may be deduced from Table 4. Several authors [e.g., refs. (*11*) and (*12*)] have used agreement between the BET surface area and the cumulative surface area from the pore-size distribution as a criterion for the validity of the pore distribution. The extreme deviation from this criterion for the G-56B, coincident with the pathological nature of this catalyst's diffusion results, implies the possibility of severe pore constrictions in the G-56B. When severe pore constrictions are present, both the mercury penetration and nitrogen desorption isotherm calculations will ascribe pore volumes to smaller radii than actually exist in the bodies of the pores. This will lead to excessive areas calculated on the basis of the pore volume–radius relationship. The same is not true of the BET surface area, and so in the presence of severe pore constrictions, the deviation should tend to be positive. The G-56B appears to be an extreme example of this type of behavior. Petersen (*13*) and Michaels (*14*) have shown theoretically that pore constrictions can have major effects on diffusion in porous materials.

TABLE 4
DEVIATIONS OF PORE DISTRIBUTION CUMULATIVE SURFACE AREAS FROM BET SURFACE AREAS

Sample No.	% Deviation $\left(\frac{S_{\text{cum}} - S_{\text{BET}}}{S_{\text{BET}}}\right) 100$
1	+14
2	−7
3	+9.3
4	+32
5	+210
6	+22
7	+20
8	+25
9	+30
10	+68
11	+27
12	+80

So it is deemed possible that the cause of the exceptions to reasonable predictability of diffusion rates may be serious constrictions in the pores.

One other point might be mentioned. There appears to be a definite converging trend in the high-pressure region of the Wakao and Smith comparison. With two exceptions—the G-56B and the ZN-0103T —the value of the (observed flux/predicted flux) tends to converge to a value of 0.7 ± 0.15. Both of the models used in this paper are based upon the assumption of cylindrical pore geometry, which is unquestionably a radical oversimplification of the pore shapes encountered in real porous media. The rate of Knudsen flow depends upon the shape of the pore, while the rate of bulk diffusion does not. For this reason, it is somewhat surprising that the Johnson and Stewart model is successful in extrapolating from a low-pressure region where Knudsen flow and pore shape effects are important into a high-pressure region where Knudsen flow and pore shape effects are relatively unimportant. For the same reason, any model which reasonably approximates the manner in which pores intersect, irrespective of the assumed shapes of the pores, would be expected to predict diffusion rates fairly well at high pressures where the Knudsen flow declines in significance. Thus a converging trend such as observed with the Wakao and Smith model is not too difficult to accept. In the lack of any really good model for predicting diffusion rates within porous materials at all pressures, the best procedure at the moment would appear to be to use the Wakao and Smith model at some very high pressure, divide the result by 1.5, and then use the Johnson and Stewart model to extrapolate this value to the desired pressure of operation. The possibilities for frequent exceptions to this method should always be borne in mind.

CONCLUSIONS

Both the Johnson and Stewart and the Wakao and Smith models of porous materials were adequate for predicting gas-phase diffusion rates to within a factor of 2 for 11 of 12 porous materials over the pressure range 1–20 atm. The only exception may have been caused by severe constrictions within the pore system.

The capability of the Johnson and Stewart model for extrapolating the diffusion rate at one pressure to that at another pressure was good, while that of the Wakao and Smith model was poor. There did, however, appear to be a tendency for the values of the (observed flux/predicted flux) from the Wakao and Smith model to converge to a common value at higher pressures. This was observed for 10 of the 12 models tested.

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