JOURNAL OF CATALYSIS 11, 195–201 (1968)

Application of the Single Pellet Reactor for Direct Mass Transfer Studies

I. Mass Transfer in Porous Media*

J. R. BALDER† AND E. E. PETERSEN‡

From the Department of Chemical Engineering, University of California, Berkeley 94720

Received January 17, 1968; revised April 29, 1968

The mass transfer behavior of a binary gas system in an alumina-supported platinum catalyst is determined from experimental studies interpreted in terms of the "dusty gas" model. The effective Knudsen diffusivities and an effective D'Arcy flow parameter are calculated from permeability measurements. The effective molecular diffusivity is calculated from a single counterdiffusion measurement. The results indicate that the diffusive behavior of the catalyst lies within the so-called intermediate region.

INTRODUCTION

The rate of a chemical reaction catalyzed by a solid depends, in part, on the total available surface area, and the activity of a catalyst generally increases with increasing surface area per unit weight. This characteristic is often obtained by creating an extensive network of very small pores within a pellet. However, to reach the active sites on which conversion occurs, the reactants must be transported from the medium surrounding the pellet through the porous structure. The resistance to high rates of mass transfer in a network of small pores can be appreciable and yet it is by means of small pores that the greatest specific surface can be produced. To assess these opposing effects of pore size on the mass transfer rate and catalytic activity and how they interact to determine the overall reaction rate of the system, an understanding of the physical processes occurring within the catalyst and the ability to represent these processes in a mathematical form are fundamental. The following experimental and theoretical work is designed to develop and to evaluate a technique for measuring directly the mass transfer and chemical reaction effects and any attendant interactions between them: the technique of the single pellet diffusive reactor.

The first part of this program involves characterizing the mass transfer for nonreacting systems. Two fundamental problems are encountered in describing mass transfer in porous media: first, the accurate mathematical representation of the physical situation and second, the evaluation of the parameters which are contained in these equations. Gunn (*1*) has given a good review of the literature on these subjects. The two most significant solutions are based either on the dusty gas model or the pseudo-capillary model.

Evans, Watson, and Mason (*2*) employed the dusty gas model to derive the flux equation for the binary diffusion of

---

* It is a pleasure to acknowledge the support of the National Science Foundation in the form of a research grant and a predoctoral fellowship (J. R. B.). The authors express their thanks to the Chevron Research Corporation for preparing and supplying the catalysts used in this investigation.

† Present address, E. I. du Pont de Nemours & Company, Wilmington, Delaware.

‡ To whom correspondence should be addressed.

gases through porous media in the absence of pressure gradients. In this model, the solid matrix is treated as a molecular species of enormous molecular weight. The results from kinetic theory for multicomponent mixtures are then applied to this ternary system containing two real gases and the "dust" molecules. By constraining the "dust" molecules to be stationary, the diffusion equations for the real gases are obtained. These equations are valid over the entire pressure range from the Knudsen region through the transition region to the normal diffusion region. The model contains no information on the actual structure of the porous medium so that the parameters appearing in these diffusion equations are the effective values and can only be determined experimentally. Under certain circumstances, measurements need only be made for a single binary gas mixture. From the values of the molecular properties as a free gas and the corresponding effective values determined experimentally, the geometric factors of the medium may be calculated. These may then be used to predict the behavior of other gas mixtures in the *same* medium for various temperatures and pressures.

The work of Pollard and Present (*3*) and Scott and Dullien (*4*) forms the basis for the pseudocapillary model. In this case, the porous medium is considered to be a collection of cylindrical capillaries. The basic diffusion equation, which is the same as that for the dusty gas model, is derived from considerations of momentum transfer between the gas and the capillary walls. Smith and his co-workers (*5*, *6*) have extended the use of the capillary model in attempts to predict the effective diffusion parameters from measurements of such structural factors as the porosity and the mean pore radius.

The objective of the present work is to predict as accurately as possible the mass transfer behavior of a specific gas system in a specific porous medium. No attempt is made to study the merits of various diffusion theories or the effects of the pore structure. The dusty gas model is employed and the effective parameters are found experimentally for each of the porous pellets.

NOMENCLATURE

c_i	Geometric factor
c_0/μ	D'Arcy flow parameter (cm²/sec torr)
C_A	Concentration of A, (g moles/cc)
$D_{K,A}$	Effective Knudsen diffusivity of A (cm²/sec)
$\mathfrak{D}_{AB}$	Effective molecular diffusivity of AB binary (cm²/sec)
$\mathfrak{D}_{AB}{}^0$	$\mathfrak{D}_{AB}P$
L	Thickness of pellet (cm)
M_A	Molecular weight of A
μ	Gas viscosity
N_A	Molar flux of A (g moles/cm² sec)
P	Total pressure (torr)
P_A	Partial pressure of A (torr)
$\bar{P}_A$	Average pressure of A within pellet (torr)
ΔP_A	Pressure drop across pellet (torr)
R_g	Universal gas constant
T	Temperature (°K)
x_A	Mole fraction of A
z	One-dimensional coordinate in pellet (cm)

EXPERIMENTAL TECHNIQUE

The equation describing the flux of gaseous molecular species in a porous medium contains several parameters which depend on the properties of the gases involved and on the internal geometric structure of the porous body. If one fits these parameters to experimental data, the behavior of this system at various conditions can be predicted. Two types of data are required in this procedure: permeability data and binary diffusion data. From the permeability data, information is obtained on the flow of a gas through the medium as a function of pressure. The diffusion data reveal the interaction of the two gas species.

A series of experiments was performed on single pellets prepared from η-alumina powder impregnated with 0.25% by weight platinum in the form of chloroplatinic acid. The powder was pressed into stainless steel support rings using the apparatus shown in Fig. 1. Both faces of the pellet were removed to a depth of approximately 0.003

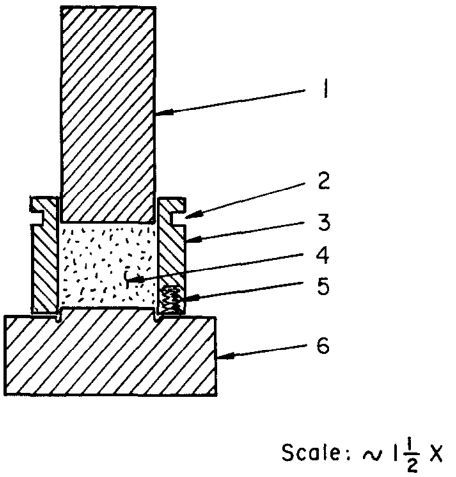

FIG. 1. Pelleting apparatus (1) ram, 0.371 in. O. D. (2) O-ring groove (3) stainless steel support ring 0.376 in. O. D. (4) catalyst powder (5) tapped for 0-80 screw (6) base.

inch in an attempt to minimize skin effects resulting from contact with the pellet die. After being heated at 300°C for 36 hr in flowing hydrogen, each of the pellets underwent a series of reaction experiments as explained in Part II (7). The macroscopic properties of the pellets are given in Table 1. Also listed is a special pellet, E, prepared from a mechanical mixture of platinum black and η-alumina (1% by weight platinum).

TABLE 1
MACROSCOPIC PROPERTIES OF CATALYST PELLETS

Pellet[a]	Die pressure (psig)	Thickness (cm)	Density (g/cc)
A	11 000	0.665	1.17
B	11 000	0.653	1.21
C	55 000	0.528	1.44
D	11 000	0.546	1.23
E	11 000	0.747	1.1

[a] *In all cases the pellet diameter was 0.955 cm.*

In the first set of experiments the permeability was measured with the apparatus shown in Fig. 2. The flow rate of a pure gas was measured as a function of the pressure drop across the pellet and the average pressure. The flow rate was measured with a bubble-type flow meter which was capable of measuring rates between approximately 1 cc/min and 50 cc/min with an error less than 2%.

The theory requires that the flow rates be extrapolated to the condition of zero average pressure. As designed, the apparatus could not be operated at average pressures less than atmospheric pressure. To provide sufficiently high average pressures for accurate extrapolations and yet maintain pressure drops within reasonable limits, a porous plug was installed downstream of the sample pellet in several runs. This second flow resistor decreased the overall flow rate but increased the average pressure in the sample pellet.

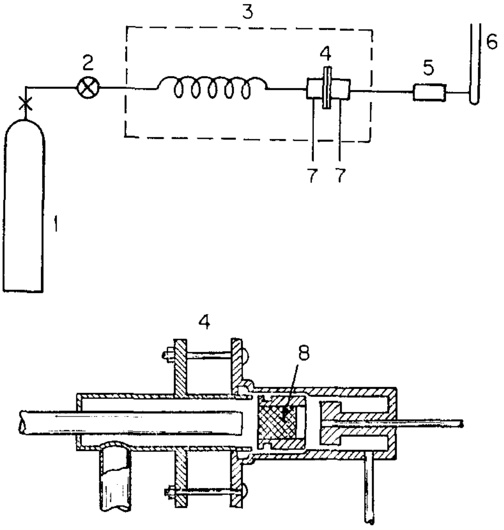

FIG. 2. Permeability apparatus (1) compressed gas cylinder (2) two-stage regulator (3) thermostated air bath (4) permeability cell (5) flow constrictor (6) bubble-type flow meter (7) pressure taps (8) sample pellet.

For Pellet B, permeabilities were determined at 55°C with argon, cyclopropane, helium, hydrogen, nitrogen, and propane. For the other pellets, measurements were usually restricted to propane. Prior to each run, the system was purged with the sample gas for at least 12 hr to ensure that no impurities were present.

In a second series of experiments the diffusion rate of a gas in a binary system at constant total pressure was measured in the apparatus shown in Fig. 3. Initially the entire system was evacuated and then filled

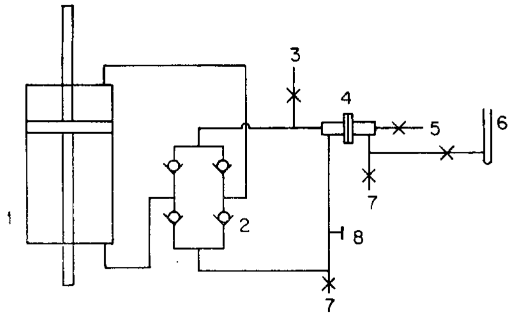

FIG. 3. Countercurrent diffusion apparatus (1) reciprocating piston pump (2) ball check valves (3) gas A inlet (4) diffusion cell (same as permeability cell of Fig. 2.) (5) gas B inlet (6) bubble-type flow meter (7) to vacuum pump (8) septum for syringe sampling.

with gas A. The piston pump recirculated this gas past one face of the pellet at approximately 60 cc/sec. Gas B was then flowed past the other face of the pellet. In most runs the flow of B was 1 cc/sec as measured by the bubble-type flow meter. The diffusion rate was determined by taking 1-cc samples of the recirculating gas at 10-min intervals with a Hamilton gas-tight syringe. A Beckman GC-2A gas chromatograph was used to analyze the concentration of gas B.*

The system was calibrated by the following technique: A known volume of gas B was injected into the system with a syringe. After recirculating the gas for several cycles, a 1-cc sample was withdrawn and analyzed. The peak height of the chromatogram could then be directly correlated with the known volume of B. This approach made it unnecessary to know the exact total volume of the system. The error in this calibration technique was less than 2%.

The following gas pairs; A and B, respectively, were studied: hydrogen and propane, helium and propane, helium and cyclopropane. In all of the runs the rate of diffusion of A out of the system was greater than that of B into the system. To maintain the diffusion cell at constant pressure, it was necessary to add small amounts of A periodically. The differential pressure across the pellet was measured with an oil-filled manometer. The reciprocating nature of the pump caused pressure cycling of ± 1 torr, but this did not have any detectable effect on the diffusion rate.

THEORETICAL CONSIDERATIONS

The one-dimensional equation for the flux of species A in a binary system through a porous medium as derived by Evans, Watson, and Mason (*2*) is

$$N_A{}^0 = \frac{-\mathfrak{D}_{AB}(dC_A/dz) + x_A(N_A{}^0 + N_B{}^0)}{1 + (\mathfrak{D}_{AB}/D_{K,A})} \tag{1}$$

The superscript 0 in the above equation implies that there is no D'Arcy flow resulting from pressure gradients and no surface flow or surface diffusion. It should be stressed that the diffusivities used are effective quantities and depend not only on the molecular species and temperature but also on the particular geometrical pore structure.

Equation (1) was modified by Gunn (*1*) to account for D'Arcy flow as follows:

$$N_A = N_A{}^0 + x_A \frac{c_0 P}{\mu} \frac{1}{R_g T} \frac{dP}{dz} \tag{2}$$

where c_0/μ is the D'Arcy parameter (cm²/sec torr). The validity of this equation can only be measured in terms of its ability to describe experimental behavior. The following relationships are also available:

$$\begin{aligned} x_A P &= P_A \\ x_B P &= P_B \\ x_A + x_B &= 1 \end{aligned} \tag{3}$$

From Eqs. (1) and (2) for each component and Eq. (3), Gunn (*1*) derived the general flux equation:

$$N_A = \left[\frac{-D_{K,A}\mathfrak{D}_{AB}{}^0}{(x_B D_{K,A} + x_A D_{K,B})P + \mathfrak{D}_{AB}{}^0}\right] \frac{P}{R_g T} \times \frac{dx_A}{dz} - \left[\frac{D_{K,A}(D_{K,B}P + \mathfrak{D}_{AB}{}^0)}{(x_B D_{K,A} + x_A D_{K,B})P + \mathfrak{D}_{AB}{}^0} + \frac{c_0 P}{\mu}\right] \frac{x_A}{R_g T} \frac{dP}{dz} \tag{4}$$

---

* Chromatograph conditions: Column; 18 ft × ¼ inch S.S. with 30% methoxyethyl adipate on Chromosorb-P, 42/60 mesh, acid-washed; temperature; 50°C; filament current: 270 mA; carrier gas: helium, approximately 40 cc/min (STP).

where $\mathfrak{D}_{AB}{}^0, = \mathfrak{D}_{AB}P$. In order to use Eq. (4), the numerical values of four effective parameters are required: $\mathfrak{D}_{AB}{}^0$, $\mathfrak{D}_{K,A}$, $\mathfrak{D}_{K,B}$, c_0/μ.

The Knudsen diffusion coefficient and the D'Arcy flow parameter are found from permeability experiments. The flow of a pure gas through the pellet is measured as a function of the average pressure within the pellet and the pressure drop across the pellet. For this case Eq. (4) reduces to

$$N_A = -\left(D_{K,A} + \frac{c_0 P}{\mu}\right)\frac{1}{R_g T}\frac{dP_A}{dz} \qquad (5)$$

After integrating over the length of the pellet, one obtains

$$N_A R_g T L/\Delta P_A = D_{K,A} + (c_0/\mu)\bar{P}_A \qquad (6)$$

According to Eq. (6), a straight line should result if the term $N_A R_g T L/\Delta P_A$ is plotted versus the average pressure. The intercept at $P = 0$ is equal to the effective Knudsen diffusion coefficient, and the slope is equal to the effective D'Arcy flow parameter.

In many cases, only a single permeability run is necessary. Values for the Knudsen diffusion coefficient of any other gas result from the relationship

$$D_{K,i} = c_1(R_g T/M_i)^{1/2} \qquad (7)$$

where M_i is the molecular weight of species i and c_1, the geometric factor. Therefore,

$$D_{K,B} = D_{K,A}(M_A/M_B)^{1/2} \qquad (8)$$

Similarly, the D'Arcy flow parameters depend only on the ratios of the gas viscosities

$$\left(\frac{c_0}{\mu}\right)_B = \left(\frac{\mu_A}{\mu_B}\right)\left(\frac{c_0}{\mu}\right)_A \qquad (9)$$

The effective molecular diffusion coefficient, $\mathfrak{D}_{AB}$, can be calculated from the rate of diffusion of gas A in gas B through the porous medium at constant total pressure. Equation (4) reduces to

$$N_A = \left[\frac{-D_{K,A}\mathfrak{D}_{AB}{}^0}{(x_A D_{K,B} + x_B D_{K,A})P + \mathfrak{D}_{AB}{}^0}\right]\frac{P}{R_g T} \times \frac{dx_A}{dz} \qquad (10)$$

The integration of this equation over the length of the pellet results in two solutions depending on the relative values of $D_{K,A}$ and $D_{K,B}$. If $D_{K,A} \neq D_{K,B}$, as is the case for most gas pairs, the solution becomes

$$N_A R_g T L = \left(\frac{D_{K,A}\mathfrak{D}_{AB}{}^0}{(D_{K,A} - D_{K,B})}\right)\ln \times \left[\frac{(D_{K,B} - D_{K,A})P x_A(1) + D_{K,A}P + \mathfrak{D}_{AB}{}^0}{(D_{K,B} - D_{K,A})P x_A(0) + D_{K,A}P + \mathfrak{D}_{AB}{}^0}\right] \qquad (11)$$

where $x_A(0)$ and $x_A(1)$ are mole fractions of A at the two faces of the pellet. If $D_{K,A} = D_{K,B}$, the solution is

$$N_A R_g T L = \frac{D_{K,A}\mathfrak{D}_{AB}{}^0 P}{D_{K,A}P + \mathfrak{D}_{AB}{}^0}[x_A(0) - x_A(1)] \qquad (12)$$

Both of the above equations require the value of $D_{K,A}$ before the molecular diffusivity can be calculated.

DISCUSSION OF RESULTS

The experimental program had two fundamental purposes. The first was to test the accuracy and consistency of the experimental permeability and diffusivity results. This was accomplished by determining the dependence of the Knudsen diffusivity and the D'Arcy flow parameter on certain molecular properties using a series of gases with differing molecular weights and viscosities and interpreting these results in the theoretical framework developed in the previous section. The second aim was to evaluate the effective parameters of several catalyst pellets for the hydrogen-propane system. In Part II a method is presented for determining the effective diffusivities through these same catalysts from reaction data for the hydrogenolysis of cyclopropane to propane. Ultimately, the effective diffusivities calculated from the physical data of this section will be compared with those calculated from the kinetic data of Part II.

Permeability Results

An example of a permeability run is shown in Fig. 4. Since the apparatus could

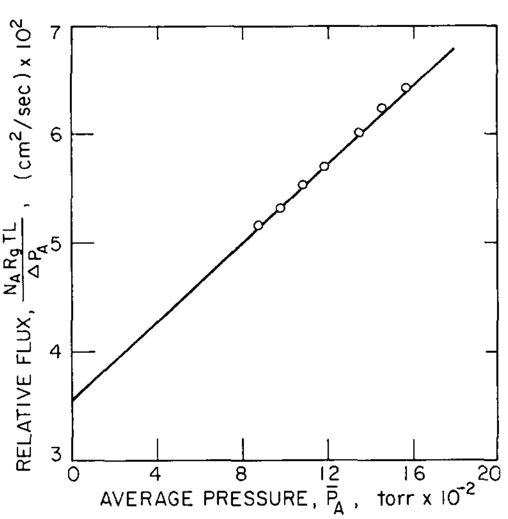

Fig. 4. Example of permeability run, propane through Pellet D.

not be operated at average pressures less than atmospheric pressure, a rather long extrapolation is required to evaluate the effective Knudsen diffusivity. In most cases, there is very little scatter in the data so that the best straight line through the data is easily found by a numerical least-squares procedure. Runs 7 and 22 listed in Table 2 were performed on the same pellet under identical conditions. The values of the Knudsen diffusivity and D'Arcy parameter for these runs indicate that the slope and intercept are reproducible within 2%.

In an attempt to justify the accuracy of the extrapolation, permeabilities were measured for a series of gases having different molecular weights. Equation (7) predicts that the Knudsen diffusivity should vary inversely with the square root of the molecular weight. The results shown in Fig. 5 verify this dependence. The dependence of the D'Arcy parameter on the gas viscosity is also shown in Fig. 5. Except for hydrogen, the data are reasonably consistent.

A complete list of the permeability results is presented in Table 2. The similarity between the effective parameters for propane and cyclopropane should be noted. This information will be important in the analysis of the reaction data in Part II.

Diffusion Results

The rate of diffusion is determined from the rate of accumulation of hydrocarbon in the recirculating gas. Experiments showed that the diffusion rate of propane is unaffected by the helium recirculation rate or flow rate of propane past the pellet face as long as one takes into account the dilution of the propane flowing past the pellet by the helium diffusing out of the

TABLE 2
Permeability Results

Run	Gas	T (°C)	μ (centipoise × 10^2)	D_K (cm^2/sec × 10^2)	c_0/μ (cm^2/sec torr × 10^5)	Pellet
5	N_2	25°	—	3.57	1.10	A
6	H_2	25°	—	13.3	2.48	A
7	N_2	55°	1.90	3.99	0.98	B
8	P	55°	0.894	3.31	1.84	B
9	H_2	55°	0.945	14.0	2.48	B
10	Ar	55°	2.43	3.51	0.64	B
11	Δ	55°	—	3.39	1.73	B
12	He	55°	2.09	10.7	0.96	B
13	P	35°	0.845	3.27	1.86	B
14	P	75°	0.943	3.20	1.84	B
15	N_2	75°	1.98	4.14	0.90	B
16	N_2	35°	1.81	3.82	0.94	B
17	P	55°	—	3.50	1.87	D
20	P	55°	—	1.34	0.271	C
21	P	45°	—	4.77	2.52	E
22	N_2	55°	—	3.92	1.00	B

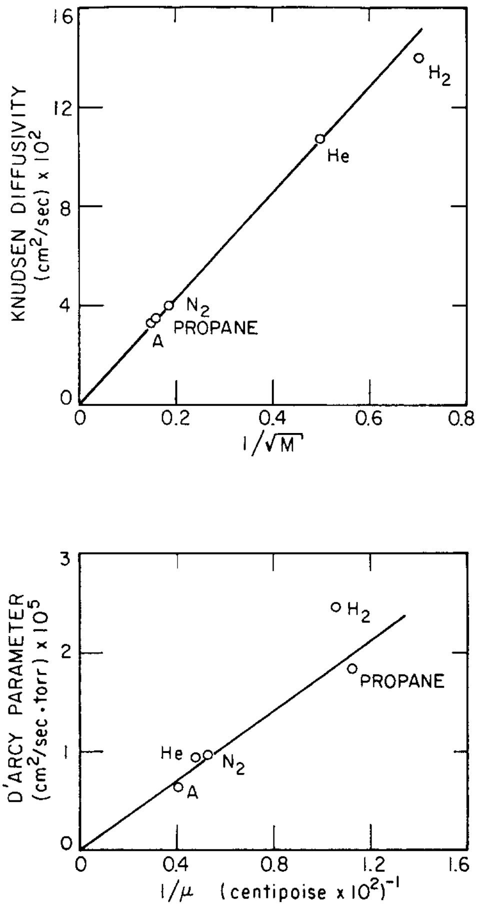

Fig. 5. Molecular weight and viscosity dependence of permeability data.

pellet (*8*). The helium flux is related to the measured propane flux as follows:

$$N_{He}/N_P = (M_P/M_{He})^{1/2} \cong 3.3$$

The following correction is applied to the propane mole fraction at the pellet face:

$$x_P(0) = (Q - N_{He})/Q \qquad (14)$$

where Q is the total gas flow rate as measured by the bubble-type flow meter.

The results of the diffusion measurements are given in Table 3. Each of the values reported is the average of two separate experiments. The maximum difference between any two experiments is 3%. These results are combined with the Knudsen diffusivities to calculate the effective molecular diffusion coefficient, $\mathfrak{D}_{HP}^0$, for the hydrogen-propane system using Eq. (11). The values are given in Table 3 and are approximately one-fourth of the free gas diffusivity, 0.45 cm³/sec.

TABLE 3
Diffusion Results[a]

Pellet	Gas pair	T (°C)	$x_P(0)$	N_P (cc/min, STP)	$\mathfrak{D}_{HP}^0$ (cm² atm/sec)
A	H_2, P	50	0.74	0.83	0.14
B	H_2, P	55	0.92	1.02	0.134
C	H_2, P	55	0.95	0.66	0.120
D	H_2, P	55	0.90	1.24	0.131
E	H_2, P	45	0.92	1.05	0.111
B	He, P	55	0.92	1.08	—
B	He, C	55	0.92	1.13	—

[a] P, propane; C, cyclopropane.

Conclusions

A rather simple experimental technique has been developed to perform accurate permeability and diffusivity measurements on single catalyst pellets. From these experiments, the effective parameters required in the mass flux equations for a binary system were evaluated. The agreement between the molecular weight dependence of the Knudsen diffusivity and kinetic theory and between the viscosity dependence of the D'Arcy flow parameter and experimental viscosities provided confidence in the form of the flux equations, the theoretical significance of the parameters, and the experimental results. Values of these effective parameters for a series of catalyst pellets form the basis for a comparison of mass transfer in reacting and nonreacting systems.

References

1. Gunn, R. D., Dissertation, University of California, Berkeley, 1967.
2. Evans, R. B., Watson, G. M., and Mason, E. A., *J. Chem. Phys.* **35**, 2076 (1961).
3. Pollard, W. G., and Present, R. D., *Phys. Rev.* **73**, 762 (1948).
4. Scott, D. S., and Dullien, F. A. L., *A. I. Ch. E. J.* **8**, 113 (1962).
5. Wakao, N., Otani, S., and Smith, J. M., *A. I. Ch. E. J.* **11**, 435 (1965).
6. Wakao, N., and Smith, J. M., *Ind. Eng. Chem. Fundamentals* **3**, 123 (1964).
7. Balder, J. R., and Petersen, E. E., **11**, 202 (1968).
8. Balder, J. R., Dissertation, University of California, Berkeley, 1967.