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Gaseous reactions in heteroporous media

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GASEOUS REACTIONS IN HETEROPOROUS MEDIA

by

ELMER ANTHONY KLAVETTER, 1959-

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ABSTRACT

A modified dusty-gas model which accounts for the effects the pore-size and tortuosity distributions have on the mass fluxes in heteroporous media is presented. The behavior of the dusty-gas model (homoporous model) can be obtained from the modified model when the pressure is either very low or very high as well as for intermediate pressures when the characteristic parameter of the introduced tortuosity function has a very small value. When the pressure is very high or very low, all pores in the porous medium are almost in a single transport regime of either molecular ~~of~~ OR Knudsen diffusion.

Comparisons of the mass fluxes predicted by the two models for binary isobaric diffusion, simultaneous diffusion and flow, and for chemical reactions with mole changes in heteroporous media show that the percentage deviations between the mass fluxes and the effectiveness factors calculated by the dusty-gas and the modified dusty-gas models can be significant. An analysis of the results indicates that the dusty-gas model could fail in predicting accurately the mass fluxes and effectiveness factors in porous systems with wide pore-size distributions, and it is suggested that the modified dusty-gas model, which incorporates the pore-size and tortuosity distributions in its constitutive equations, should be appropriate for use in the design and prediction of the performance of separation and reaction systems involving porous media required to operate in the transition transport regime.

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COMPARISON OF MASS FLUXES PREDICTED BY THE DUSTY-GAS AND A MODIFIED DUSTY-GAS MODEL

by

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ABSTRACT

The equations of the dusty-gas model (homoporous model) are modified through the use of correction factors which account for the effects the pore-size and tortuosity distributions have on the mass fluxes in heteroporous media. When the correction factors approach unity, the modified dusty-gas model approaches the behavior of the dusty-gas equations; this occurs when the pressure of the system is either very low or very high because, at either extreme, almost all pores in a porous medium are in a single transport regime, that is either Knudsen or molecular diffusion.

A comparison of the mass fluxes predicted by the modified dusty-gas (heteroporous model) and the dusty-gas models for binary isobaric diffusion and simultaneous flow and diffusion, shows that the percentage deviation between N_{iMDG} and N_{iDG} (i = species A or B) may be, in some cases, significant (up to 75% for the porous media studied in this work); this indicates that the dusty-gas model (homoporous model) could fail in predicting accurately the mass fluxes in porous media with wide pore-size distributions. The percentage deviation in the mass fluxes becomes smaller as the pressure increases above certain values at which the deviation of the correction factors from unity is small.

INTRODUCTION

The dusty-gas model has been developed [1-5] to describe mass transfer in homoporous media and it has a firmer theoretical basis than other current models [6]. It takes into account pore geometry and also the transport regime, and correctly combines the simultaneous effects of ordinary molecular diffusion and Knudsen diffusion in the transition region and reduces to the correct asymptotic forms under conditions of very low and high pressures. A number of researchers [7-9] have used the dusty-gas model to describe reaction and simultaneous diffusion in porous media.

Deviations between experimental fluxes and those computed through the use of the dusty-gas model have been observed [10-12] in bimodal structures. These deviations indicate that the nonuniformity of the porous structures may prohibit the application of the dusty-gas model to bimodal media.

The work reported here, presents the theoretical results of a modified form of the dusty-gas model for heteroporous media, and compares these results with those obtained from the dusty-gas model which describes homoporous media.

MATHEMATICAL MODELING

The Dusty-Gas Model (Homoporous Media)

The dusty-gas equation [2,3,5] for component A in a binary system of A and B has the form,

$$N_A = \frac{-C_2 D^o{}_{AB}\ K_A P}{(C_2 D^o{}_{AB} + P\ K_m) R_g T} \nabla Y_A - \left(\frac{(C_2 D^o{}_{AB} + P\ K_B) K_A}{C_2 D^o{}_{AB} + P\ K_m} + \frac{C_o P}{\mu_m}\right) \frac{Y_A}{R_g T} \nabla P \qquad (1)$$

where

$$K_A = C_1 (R_g T/M_A)^{1/2} \qquad (2)$$

$$D^o{}_{AB} = P\ D_{AB} \qquad (3)$$

$$K_m = Y_B K_A + Y_A K_B \qquad (4)$$

The flux equation for component B has a form similar to that of species A with appropriate changes for the mole fraction, mole fraction gradient, and the numerators of the terms which involve K_A and K_B [3,5].

The first term on the right-hand side of Equation (1) represents the diffusional contribution resulting from a concentration gradient whereas the last two terms represent the flux contribution due to a total pressure gradient. The first subgroup in the pressure gradient term represents the slip-flow contribution and the second one represents the D'Arcy-flow contribution.

The three constants C_o, C_1, and C_2 depend only upon the structure of the porous media and are independent of the type of experiment and of experimental conditions, and also independent of the flowing fluids. C_o is the viscous permeability constant, with dimensions of length squared. C_1 is the Knudsen permeability constant, with dimensions of length, and C_2 is the geometric factor for diffusion, which is dimensionless.

Equation (1) can be written for convenience in the following form:

$$N_A = -Q_{DA} \frac{P}{R_g T} \nabla Y_A - (Q_{SA} + Q_{VA}) \frac{Y_A}{R_g T} \nabla P \tag{5}$$

where

$$Q_{DA} = (C_2 D^o{}_{AB} K_A)/(C_2 D^o{}_{AB} + K_m P) \tag{6}$$

$$Q_{SA} = (K_A (C_2 D^o{}_{AB} + P K_B))/(C_2 D^o{}_{AB} + P K_m) \tag{7}$$

$$Q_{VA} = (C_o P)/\mu_m \tag{8}$$

Q_{DA} and Q_{SA} are, respectively, the diffusion-flow and slip-flow coefficients of component A, and the viscous flow coefficient is Q_{VA}.

The dusty-gas model [1-5] can only describe the transport behavior of homporous media in which the relative flux contribution of any pore is the same in all situations since all pores behave uniformly. The transport behavior of a homoporous medium is very much like that in a cylindrical pore with constant diameter [5,11]. The mass transfer mechanism shifts from the Knudsen regime to the transition region and finally to the molecular regime as the pressure increases. Thus, the transport coefficients are different for different operating conditions. For a heteroporous medium, however, the relative flux contribution from pores with a particular size is different at different operating conditions, and the transport coefficients and the mass transfer mechanisms are functions of the operating conditions as well as of the pore-size distribution. Thus, the varying relative flux contribution of any particular size of pores in a heteroporous medium is the principal cause [10-12] for deviations in applying the dusty-gas model to catalysts with a wide ranging pore-size distribution.

The Modified Dusty-Gas Model (Heteroporous Media)

An expression for the average transport coefficient of a set of parallel cylindrical pores, each having the same length but a different diameter, has been constructed by Wendt et al. [13]. Their expression for a system with identical pores and moderate non-linear concentration gradients can be represented by the following form [12] which is appropriate for many situations in practice,

$$T'_{avg} = \frac{\sum_{R=o}^{\infty} (T'(R)V(R))}{\sum_{R=o}^{\infty} V(R)} \tag{9}$$

where T'(R) is the transport coefficient of pores with radius, R, and V(R) is the volume percent of pores with radius, R.

We use Equation (9) here, to describe the transport coefficient of a differential segment in one-dimensional heteroporous medium. The differential segment can be considered as a collection of noninter-connected cylinders having a distribution of sizes. The pores in the real heterporous system [14-16] are not usually parallel and T'_{avg} will also be a function of their tortuosity factors. Thus, a better form for T'_{avg} is given by,

$$T'_{avg} = \frac{\sum_{R=o}^{\infty} (T'(R)V(R)\Delta(R))}{\sum_{R=o}^{\infty} (V(R)\Delta(R))} \tag{10}$$

where

$$\Delta(R) = 1/(\tau^2(R)). \tag{11}$$

In a real porous structure, smaller pores are generally more tortuous than the larger ones [14-16], and this is related to the fact that the smaller pores generally have larger length to diameter ratios than the larger pores, implying that the average tortuosity factor of small pores is greater than that of large ones.

There is no theory available or data regarding the correlation between tortuosity factor and pore size in a heteroporous medium. Using the experimental evidence [15,16] as a basis, it is assumed that the tortuosity factor decreases continuously and monotonically to an asymptotic value as the pore radius increases, implying that $\Delta(R)$ is a continuous monotonically increasing function of the pore radius. The function $\Delta(R)$ appears in the same form in both the numerator and denominator of Equation (10) and we thus say that $\Delta(R)$ reaches a normalized asymptotic value of unity as pore radius increases.

The shape of $\Delta(R)$ is expected to be exponential [12,15,16] and should be different for different heteroporous media. The following expression is postulated as the relation between the $\Delta(R)$ and pore size,

$$\Delta(R) = 1 - \exp(-\alpha R) \tag{12}$$

which qualitatively satisfies the expected form. The shape of $\Delta(R)$ is determined by the characteristic parameter α of the porous structure, which may be determined by fitting the theoretical predictions of the modified dusty-gas model to the experimental data obtained for the given heteroporous medium. It should be noted that Equation (10) implies that the transport coefficients of a porous system can be represented by the effective volume mean value of the transport coefficients for individual pores since $(V(R)\Delta(R))$ can be considered as the effective volume for mass transfer.

When the dusty-gas model is applied to systems which have a wide ranging pore-size distribution, it averages the experimental data in such a way as to represent a hypothetical homoporous system corresponding to the real heteroporous system. Then the effective volume mean pore radius of a heteroporous system may represent the pore size of the hypothetical homoporous system. Thus the transport coefficients obtained by fitting the dusty-gas model to experimental data are equivalent [12] to the values for a homoporous system with the effective volume mean pore radius as the pore size. Since the actual coefficient should be equivalent to the effective volume mean coefficient for the pores in the heteroporous medium [11-13], correction factors of heteroporosity should multiply the transport coefficients in the dusty-gas model for systems with wide ranging pore-size distributions. These correction coefficients may be defined as the ratio of the effective volume mean transport coefficients to the transport coefficients at volume mean pore radius.

Then the diffusion and slip flow correction factors ϕ_{DA}, ϕ_{DB}, ϕ_{SA} and ϕ_{SB} have the following forms:

$$\phi_D = \phi_{DA} = \phi_{DB} = \frac{((\sum_{R=o}^{\infty} Q'_{DA}(R)V(R)\Delta(R))/(\sum_{R=o}^{\infty} V(R)\Delta(R)))}{Q'_{DA}(R_m)} \tag{13}$$

$$\phi_{SA} = \frac{((\sum_{R=o}^{\infty} Q'_{SA}(R)V(R)\Delta(R))/(\sum_{R=o}^{\infty} V(R)\Delta(R)))}{Q'_{SA}(R_m)} \tag{14}$$

$$\phi_{SB} = \frac{((\sum_{R=o}^{\infty} Q'_{SB}(R)V(R)\Delta(R))/(\sum_{R=o}^{\infty} V(R)\Delta(R)))}{Q'_{SB}(R_m)} \tag{15}$$

In Equations (13-15), the superscript (') indicates the cylindrical pore and R_m is the effective volume mean pore radius given by the expression,

$$R_m = \frac{\sum_{R=o}^{\infty} RV(R)\Delta(R)}{\sum_{R=o}^{\infty} V(R)\Delta(R)} \tag{16}$$

The transport coefficients of cylindrical pores, $Q'_{DA}(R)$, and $Q'_{SA}(R)$, have the following forms [2,17-19]

$$Q'_{DA}(R) = \frac{K'_A(R)\ D^o_{AB}}{D^o_{AB} + P\ K'_m(R)} \tag{17}$$

$$Q'_{SA}(R) = \frac{(D^{o}_{AB} + K'_{B}(R)P)K'_{A}(R)}{D^{o}_{AB} + PK'_{m}(R)} \qquad (18)$$

$$K'_{A}(R) = \frac{2}{3}R\,(\frac{8R_{g}T}{\pi M_{A}})^{1/2} \qquad (19)$$

$$K'_{B}(R) = \frac{2}{3}R\,(\frac{8R_{g}T}{\pi M_{B}})^{1/2} \qquad (20)$$

$$K'_{m}(R) = K'_{B}(R)Y_{A} + K'_{A}(R)Y_{B} \qquad (21)$$

$Q'_{DB}(R)$ and $Q'_{SB}(R)$ are given by similar forms as those shown in Equations (17-18) with appropriate interchanges of $K'_{A}(R)$ and $K'_{B}(R)$ [19].

The modified dusty-gas equation for component A in a binary system of A and B is as follows:

$$N_{A} = -\phi_{D}Q_{DA}\frac{P}{R_{g}T}\nabla Y_{A} - (\phi_{SA}\,Q_{SA} + Q_{VA})\frac{Y_{A}}{R_{g}T}\nabla P \qquad (22)$$

There is no correction for the viscous flow coefficient since only one mechanism governs mass transfer of this type and thus, the relative viscous flow contribution from pores of a particular size is the same in all situations [19]. The heteroporosity correction factors in Equation (22) account for the pore-size and tortuosity distribution effects on mass flux but still the modified dusty-gas model relies on C_o, C_1, and C_2 to characterize the porous structure in addition to those effects.

The parameters C_o, C_1, C_2 and α in the modified dusty-gas model can be estimated from experimental data obtained from steady-state permeability and binary isobaric diffusion experiments, and fitted to the equations of the modified dusty-gas model. These experiments can be conducted relatively quickly [5,11,12].

The theoretical predictions of the dusty-gas model and of the modified dusty-gas model are compared for two systems of operating conditions,

(a) Binary Isobaric Diffusion, and

(b) Simultaneous Diffusion and Flow.

The binary system consists of Nitrogen and Helium and Nitrogen is taken to be component A and Helium is component B. The data used in the calculations for this binary system are given in Table 1. In the next two sections the equations used in the calculations of binary isobaric diffusion, and simultaneous diffusion and flow, are presented.

Binary Isobaric Diffusion

Equation (22) for one-dimensional isobaric diffusion takes the form,

$$N_A = - \frac{\phi_D C_2 D^o{}_{AB} \, K_A P}{(C_2 \, D^o{}_{AB} + K_m P) R_g T} \, \frac{dY_A}{dx} \tag{23}$$

with the following boundary conditions:

$$\text{at } x = o,\ Y_A = Y_{A_o} \tag{24}$$

$$\text{at } x = L,\ Y_A = Y_{A_L} \tag{25}$$

The integrated form of Equation (23) for a constant flux system gives,

$$N_A = \frac{\phi_D\ C_2 D^o{}_{AB}}{R_g T L \theta_A} \ln \left[\frac{1-\theta_A Y_{A_L} + C_2 D^o{}_{AB}/(PK_A)}{1-\theta_A Y_{A_o} + C_2 D^o{}_{AB}/(PK_A)}\right] \tag{26}$$

where

$$\theta_A = 1 + \frac{N_B}{N_A} = 1 - (\frac{M_A}{M_B})^{1/2} \tag{27}$$

The flux equation for species A in the dusty-gas model, is obtained from Equation (26) by setting $\phi_D = 1.0$.

Simultaneous Diffusion and Flow

The pressure and concentration gradients for one dimensional simultaneous diffusion and flow can be written, using the procedure in [11], as follows:

$$\frac{dP}{dx} = - \frac{aN_B + a'N_A}{ab' + a'b} \tag{28}$$

$$\frac{dY_A}{dx} = - \frac{bN_B - b'N_A}{ab' + a'b} \tag{29}$$

where

$$a = \frac{\phi_D C_2 D^o_{AB} K_A P}{(C_2 D^o_{AB} + P K_m) R_g T} \tag{30}$$

$$b = \frac{Y_A}{R_g T}\left[\frac{\phi_{SA} K_A (C_2 D^o_{AB} + P\, K_B)}{C_2 D^o_{AB} + P\, K_m} + \frac{P C_o}{\mu_m}\right] \tag{31}$$

$$a' = \frac{\phi_D C_2 D^o_{AB} P K_B}{R_g T (C_2 D^o_{AB} + P K_m)} \tag{32}$$

$$b' = \frac{Y_B}{R_g T}\left[\frac{\phi_{SB} K_B (C_2 D^o_{AB} + P K_A)}{C_2 D^o_{AB} + P K_m} + \frac{P C_o}{\mu_m}\right] \tag{33}$$

The boundary conditions for Equations (28) and (29) are,

$$\text{at } x = o,\ P = P_o,\ Y_A = Y_{A_o} \tag{34}$$

$$\text{at } x = L,\ Y_A = Y_{A_L},\ P = P_L \tag{35}$$

Dividing Equation (28) by Equation (29) a direct relationship between P and Y_A is obtained,

$$\frac{dP}{dY_A} = -\frac{a + a'\,(N_A/N_B)}{b - b'\,(N_A/N_B)} \tag{36}$$

The boundary conditions for Equation (36) are given by Equations (34) and (35). The unknown variables N_A and N_B are determined through the use of a procedure similar to that developed in [11] for the dusty-gas model; it should be noted, though, that for the modified dusty-gas model the correction factors ϕ_D, ϕ_{SA}, and ϕ_{SB} vary along the path of diffusion and flow, that is, between x = o and x = L.

The solution procedure is as follows:

1. The parameters C_o, C_1, C_2 and α, obtained from permeability and isobaric diffusion experiments, are used in Equations (28) - (36).

2. Integration of Equation (36) is performed, using a sixth-order Runge-Kutta method [22], from $Y_A = Y_{A_o}$ and $P = P_o$ to Y_{A_L} with a guessed value of $w = (N_A/N_B)$. The integration provides a computed value of pressure, P_{L_c}, at $Y_A = Y_{A_L}$. This is an interative process and is determined when $\left|\frac{(P_{L_c} - P_L)}{P_L}\right| < 10^{-8}$. Successive values of w are obtained by a simple bisection method [22].

3. By guessing N_A to obtain $N_B = N_A/w$, Equations (28) and (29) are integrated (with a sixth order Runge-Kutta method) simultaneously from x = o, $Y_A = Y_{Ao}$ and $P = P_o$ to z = L, giving a computed pressure, P_{L_c}, and a computed composition, $Y_{A_{L_c}}$ at z = L. In this iterative process, N_A is determined when $\left|(P_{L_c} - P_L)/P_L\right| < 10^{-8}$.

4. The viscosity of the gaseous mixture, μ_m, is computed from viscosities of pure components [19], using the following expression,

$$\mu_m = \frac{\mu_A Y_A M_A^{1/2} + \mu_B Y_B M_B^{1/2}}{Y_A M_A^{1/2} + Y_B M_B^{1/2}} \qquad (37)$$

Detailed computer calculations [22] have shown that in Equation (21) the arithmetic average values of Y_A and Y_B at $x = o$ and $x = L$ may be used instead of the local values, with insignificant changes in the values of ϕ_D, ϕ_{SA}, and ϕ_{SB}. The sums in Equations (13) - (16) were replaced by integrals, and the integrations were obtained by applying Simpson's rule of integration.

The fluxes N_A and N_B for the dusty-gas model can be obtained from the procedure described above by setting $\phi_D = \phi_{SA} = \phi_{SB} = 1.0$ in Equations (28) - (36).

RESULTS AND DISCUSSION

In Figure 1 the shape of the V(R) functions for two different porous catalysts [23] are shown, and it is seen that $V_2(R)$ provides a more dispersed distribution relative to that obtained from $V_1(R)$. The dependence of $\Delta(R)$ on the characteristic parameter α is shown in Figure 2. For small values of α the volume percentage of pores with $\Delta(R)$ less than unity is significant, and thus the values of the correction factors are influenced substantially by the dispersed nature of $\Delta(R)$ at small values of α. For large values of α the volume percentage of pores with $\Delta(R)$ less than unity may be negligible and Equation (9) should be a good approximation in estimating average transport coefficients.

Figures 3-6 show the diffusion and slip-flow correction factors as functions of pressure for both pore volume distributions $V_1(R)$ and $V_2(R)$. It is seen that the correction factors reach unity when the pressure is either very low or very high because, at either extreme, almost all pores in a porous medium are in a single transport regime, that is either Knudsen or molecular diffusion. Thus, the dusty-gas model should be applicable, without correction, to any porous medium at either pressure extreme.

In Figure 3, it is seen that for the larger values of $\alpha(1.0 \times 10^{-2}, 2.0 \times 10^{-4})$, the diffusion-flow correction factor of the porous structure with the $V_1(R)$ distribution deviates from unity more than the correction factor of the porous medium whose distribution is $V_2(R)$, while the opposite occurs for $\alpha = 1.0 \times 10^{-8}$. The deviations of the slip-flow correction factors from unity, Figure 4-5, decrease as the value of α decreases. In Figure 5, the porous medium whose pore-size distribution is given by $V_2(R)$ reaches the molecular regime at higher pressures, than that with the $V_1(R)$ distribution. In the other case as it is shown in Figure 4, the porous structure with the $V_2(R)$ distribution reaches the molecular regime at lower pressures, than that with the $V_1(R)$ distribution, while the Knudsen regime is reached at lower pressures by the porous medium with the $V_1(R)$ distribution. It should be emphasized that these observations of the particular systems examined cannot be generalized since the evaluation of the correction factors depends on the product $V(R)\Delta(R)$ instead of either $V(R)$ or $\Delta(R)$, and therefore each given porous medium should have its own particular functional forms for its correction factors, except at very low and very high pressures, since then the correction factors for any porous medium are very close to unity.

In Table 2, the computed mass fluxes for component A by the modified dusty-gas and the dusty-gas models are shown for the case of binary isobaric diffusion; the values used for C_1 and C_2 are characteristic of industrial porous catalysts [11]. The values of $N_{B_{MDG}}$ and $N_{B_{DG}}$ can be easily obtained by using the data in Table 2 and Equation (27). It is seen that for all values of α and for both porous structures, the percentage deviation in the fluxes decreases monotonically as the pressure increases, and this follows from the fact that at very large pressures the correction factors approach unity. The results in Table 2 also show that the percentage deviations for $\alpha = 1.0 \times 10^{-8}$ and $\alpha = 1.0 \times 10^{-10}$, for both pore-size distributions, differ by insignificant amounts. It should be noted that while the percentage deviation in the fluxes is rather small for values of α in the range 10^{-6} - 10^{-10}, this is not the case for the larger values of α in the usual operating pressure conditions in practice, as the results indicate. The results in Table 2 show that the values of C_1, C_2, and C_0 and α should be obtained simultaneously from permeability [12] and isobaric diffusion experiments, since in effect the correction factors estimated through $\Delta(R)$ will eliminate the discrepancy between C_1 values from permeability and from isobaric diffusion experiments [12], which has been the case when the dusty-gas model is used [11,12]. It should be noted that when the dusty-gas model is used, its parameters C_0 and C_1 are obtained from permeability experiments [11], while C_1 and C_2 are obtained from binary isobaric diffusion experiments [5,11]. The value of C_1 obtained from permeability experiments is usually different than that obtained from isobaric diffusion experiments [12], since all pores do not have the same length or have the same contribution to the transport flux. The correction factors of the modified dusty-gas model will eliminate this discrepancy.

Extensive calculations for the case of binary isobaric diffusion have shown that for constant values of α, P, and C_1, the percentage change of N_A as C_2 varies from 0.1 to 0.8, is approximately the same for both the dusty-gas and the modified dusty-gas models [22]. However, the magnitude of the change in N_A over the range $0.1 \leq C_2 \leq 0.8$, can differ by up to 50%-60% of the change in the value of N_A in the modified dusty-gas model with respect to that in the dusty-gas model. Similar results were obtained when α, P, and C_2 were kept constant and C_1 varied from 50×10^{-8} to $2{,}000 \times 10^{-8}$ [22].

In Table 3 the calculated mass fluxes of components A and B by the modified dusty-gas and the dusty-gas models are shown for the case of simultaneous diffusion and flow; the values of C_0, C_1, C_2 and ΔP are representative of porous media used in industry [11]. One can observe that for values of α in the range 10^{-6} to 10^{-10} and for both pore-size distributions, the percentage deviation in the fluxes is rather small; this is not the case for $\alpha = 1.0 \times 10^{-2}$ and $\alpha = 2.0 \times 10^{-4}$ where percentage deviations up to approximately 75% are obtained. Again, the percentage deviation in the fluxes decreases as the pressure increases, since at higher pressures the correction factors ϕ_D, ϕ_{SA}, and ϕ_{SB} approach unity. The results shown in this table, indicate that for porous catalysts with wide pore-size distributions and whose pores do not have the same length, the dusty-gas model will predict fluxes which are always larger than those of the modified dusty-gas model which accounts for the pore-size distribution and the varying lengths of the pores through its correction factors.

Extensive computations [22] have shown that variations in ΔP, C_o, C_1 and C_2 have significant effects on the values of N_A and N_B for both the dusty-gas and the modified dusty-gas models.

CONCLUSIONS AND REMARKS

The correction factors defined in Equations (13) - (15) establish a modified dusty-gas model which should be applicable in predicting mass transfer in porous media with wide pore-size distributions. The correction factors reach unity when the pressure is either very low or very high, since at either extreme, essentially all pores in a porous medium are in a single transport regime, either Knudsen or molecular. Therefore, the dusty-gas model should be applicable without correction to any porous medium at either pressure extreme. For large values of α the function $\Delta(R)$ has almost a constant value, equal to unity, and Equation (9) may be a good approximation for estimating average mass transport coefficients and the correction factors. The use of the function $\Delta(R)$ is an attempt to incorporate in the mass flux equation, the fact [15,16] that in a real porous structure smaller pores are generally more tortuous than the larger ones, and therefore, all pores do not have the same contribution, based on the volume, to the transport flux.

A comparison of the fluxes predicted by the modified dusty-gas (heteroporous model) and the dusty-gas (homoporous model) models, for isobaric diffusion and simultaneous flow and diffusion, shows that the dusty-gas model always predicts larger fluxes than those estimated from the modified dusty-gas model. The percentage deviation between $N_{i_{MDG}}$ and $N_{i_{DG}}$ ($i = A,B$) may be, in some cases, significant (up to 75% for the porous media studied in this work); the results on the fluxes show that significant deviations between experimental data of mass transport in heteroporous media and those predicted by the dusty-gas model may occur as indeed, it has been the case [10-12]. The percentage deviation in the mass fluxes becomes smaller as the pressure increases above certain values at which the deviation of the correction factors ϕ_D, ϕ_{SA}, and ϕ_{SB} from unity is small, and then the modified dusty-gas model approaches the behavior of the dusty-gas equations. The modified dusty-gas model transforms the dusty-gas equations into forms applicable for describing mass transport in heteroporous structures.

It would be of interest to investigate the effect that such deviations in the mass fluxes, have on the rates of reactions which occur in porous catalysts with wide pore-size distributions.

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NOTATION

a, a' ≡ defined by Equations (30) and (32), respectively, g-mole/cm-sec

b, b' ≡ defined by Equations (31) and (33), respectively, g-mole-cm/dyn-sec

C_0 ≡ constant dependent only upon structure of porous medium and giving relative D'Arcy flow permeability, cm^2

C_1 ≡ constant dependent only upon structure of porous medium and giving relative Knudsen flow permeability, cm

C_2 ≡ constant dependent only upon structure of porous medium and giving ratio of molecular diffusivity within the porous medium to the free gas diffusivity, dimensionless

D_{AB} ≡ free gas mutual diffusivity in a binary mixture of A and B, cm^2/sec

K_A ≡ effective Knudsen diffusivity of A, cm^2/sec

$K'_A(R)$ ≡ Knudsen diffusivity of A in a cylindrical pore with radius, R, cm^2/sec

K_m ≡ effective Knudsen diffusivity of a gas mixture, cm^2/sec

L ≡ length of catalyst pellet, cm

M_A ≡ molecular weight of A, g/g-mole

M_B ≡ molecular weight of B, g/g-mole

N_A ≡ molar flux of A, $g\text{-}mole/cm^2\text{-}sec$

P ≡ total pressure, dyn/cm^2

P_o ≡ total pressure at x = o, dyn/cm^2

P_L ≡ total pressure at x = L, dyn/cm^2

$Q'_{DA}(R)$ ≡ diffusion-flow coefficient of A in a cylindrical pore with radius, R, cm^2/sec

R ≡ pore radius, Å

R_g ≡ gas constant, 8.317×10^7 erg/g-mole-°K

T ≡ absolute temperature, °K

T'(R) ≡ transport coefficient of pores with radius, R, cm^2/sec

T'_{avg} ≡ average transport coefficient of porous medium, cm^2/sec

V(R) ≡ volume percent of pores with radius, R, dimensionless

w ≡ flux ratio of A to B, dimensionless

Y_A ≡ mole fraction of A, dimensionless

Y_B ≡ mole fraction of B, dimensionless

x ≡ distance in the direction of mass transfer, cm

GREEK LETTERS

α ≡ characteristic parameter of function $\Delta(R)$, $Å^{-1}$

$\Delta(R)$ ≡ effectiveness function of pores with radius, R, in porous medium, defined by Equation (12), dimensionless

μ_A ≡ viscosity of A, g/cm-sec

$\tau(R)$ ≡ tortuosity factor of pores with radius, R, in porous medium, dimensionless

ϕ_D ≡ diffusion-flow correction factor, dimensionless

ϕ_{SA} ≡ slip-flow correction factor of A, dimensionless

SUBSCRIPTS

A ≡ component A

avg ≡ avgerage

B ≡ component B

C ≡ calculated value

D ≡ diffusion-flow

DG ≡ dusty-gas model

m ≡ mixture, or volume mean value

MDG ≡ modified dusty-gas model

S ≡ slip flow

1 ≡ porous medium 1

2 ≡ porous medium 2

TABLE HEADINGS

Table 1. Data of the Binary System

Table 2. Predicted Mass Fluxes for Component A by the Modified Dusty-Gas and the Dusty-Gas Models; Binary Isobaric Diffusion.

Table 3. Predicted Mass Fluxes for Components A and B by the Modified Dusty-Gas and the Dusty-Gas Models; Simultaneous Diffusion and Flow.

TABLE 1

Data of the Binary System

$M_A = 28.01$, $M_B = 4.00$, $T = 299.3$, $L = 0.63$, $Y_{A_o} = 0.03$, $Y_{A_L} = 0.96$

$\mu_A = 0.14 \times 10^{-6} P + 177.80 \times 10^{-6}$

Ref. [20]

$\mu_B = 196.10 \times 10^{-6}$

D^o_{AB} = is calculated using the correlation in Ref. [21]

Range of Values for C_o, C_1, C_2 α, P_o, and ΔP Used in Calculations

---

$C_o = 25 \times 10^{-12} - 1{,}000 \times 10^{-12}$

$C_1 = 50 \times 10^{-8} - 2{,}000 \times 10^{-8}$

$C_2 = 0.1 - 0.8$

$\alpha = 10^{-2} - 10^{-10}$

$P_o = 1 - 10$ (Atm)

$\Delta P = P_o - P_L = 0.05 - 0.13$ (Atm)

TABLE 2

Predicted Mass Fluxes for Component A by the Modified Dusty-Gas and the Dusty-Gas Models; Binary Isobaric Diffusion

		$V_1(R)$		$V_2(R)$	
α	P(Atm)	$N_{A_{MDG}} \times 10^5$	%DEV N_A	$N_{A_{MDG}} \times 10^5$	%DEV N_A
1.0×10^{-2}	1	0.34	66.46	0.81	20.02
	6	0.80	40.69	1.26	5.87
	10	0.93	32.63	1.32	3.82
	14	1.01	27.56	1.35	2.83
	20	1.09	22.56	1.37	2.05
2.0×10^{-4}	1	0.75	26.10	0.90	10.70
	6	1.19	10.78	1.30	2.54
	10	1.27	7.84	1.35	1.59
	14	1.30	6.25	1.37	1.16
	20	1.33	4.85	1.39	0.83
1.0×10^{-6}	1	0.98	2.29	0.98	2.47
	6	1.33	0.82	1.33	0.52
	10	1.37	0.58	1.37	0.32
	14	1.38	0.46	1.39	0.23
	20	1.40	0.35	1.40	0.16
1.0×10^{-8}	1	0.99	1.86	0.99	2.25
	6	1.33	0.66	1.33	0.47
	10	1.37	0.47	1.37	0.29
	14	1.39	0.37	1.39	0.21
	20	1.40	0.28	1.40	0.15
1.0×10^{-10}	1	0.99	1.86	0.99	2.25
	6	1.33	0.66	1.33	0.47
	10	1.37	0.47	1.37	0.29
	14	1.39	0.37	1.39	0.21
	20	1.40	0.28	1.40	0.15

All of the above results were obtained with $C_1 = 2000 \times 10^{-8}$ and

$$C_2 = 0.5; \quad \%\text{DEV } N_A = \frac{N_{A_{DG}} - N_{A_{MDG}}}{N_{A_{DG}}} \times 100$$

TABLE 3

Predicted Mass Fluxes for Components A and B by the Modified Dusty-Gas and the Dusty-Gas Models; Simultaneous Diffusion and Flow

		$V_1(R)$				$V_2(R)$			
α	P_o(Atm)	$N_{A_{MDG}} \times 10^5$	$N_{B_{MDG}} \times 10^5$	%DEV N_A	%DEV N_B	$N_{A_{MDG}} \times 10^5$	$N_{B_{MDG}} \times 10^5$	%DEV N_A	%DEV N_B
1.0×10^{-2}	1	0.22	1.18	74.78	59.53	0.67	2.38	23.07	18.30
	2	0.36	1.64	64.77	51.97	0.88	3.00	15.13	12.11
	5	0.56	2.37	50.36	38.75	1.03	3.64	7.96	6.11
	10	0.66	3.01	39.73	27.94	1.05	4.04	4.71	3.30
2.0×10^{-4}	1	0.59	2.17	32.49	25.76	0.76	2.62	12.78	10.14
	2	0.78	2.75	24.12	19.31	0.95	3.21	7.63	6.11
	5	0.95	3.42	15.40	11.83	1.08	3.77	3.64	2.80
	10	0.98	3.86	10.64	7.46	1.08	4.11	2.04	1.43
1.0×10^{-6}	1	0.84	2.83	3.84	3.04	0.85	2.85	3.01	2.38
	2	1.00	3.34	2.67	2.13	1.02	3.37	1.67	1.33
	5	1.10	3.83	1.59	1.22	1.11	3.85	0.76	0.58
	10	1.09	4.14	1.08	0.75	1.10	4.16	0.42	0.29
1.0×10^{-8}	1	0.84	2.84	3.39	2.68	0.85	2.85	2.77	2.20
	2	1.01	3.35	2.34	1.87	1.02	3.37	1.55	1.24
	5	1.11	3.83	1.41	1.08	1.11	3.85	0.70	0.54
	10	1.09	4.15	0.93	0.65	1.10	4.16	0.38	0.26
1.0×10^{-10}	1	0.84	2.84	3.39	2.68	0.85	2.85	2.77	2.20
	2	1.01	3.35	2.34	1.87	1.02	3.37	1.55	1.24
	5	1.11	3.83	1.41	1.08	1.11	3.85	0.70	0.54
	10	1.09	4.15	0.93	0.65	1.10	4.16	0.38	0.26

All of the above results were obtained with $C_o = 25 \times 10^{-12}$, $C_1 = 2000 \times 10^{-8}$, $C_2 = 0.5$, and

$$\Delta P = P_o - P_L = 0.053(\text{Atm}); \quad \%\text{DEV } N_i = \frac{N_{i_{DG}} - N_{i_{MDG}}}{N_{i_{DG}}} \times 100 \text{ for } i = A, B$$

FIGURE CAPTIONS

Figure 1. Pore-Size Distributions of Porous Media 1 and 2.

Figure 2. Dependence of the Effectiveness Function $\Delta(R)$ on the Characteristic Parameter α.

Figure 3. The Effect of Pressure on the Diffusion-Flow Correction Factors.

1 $\equiv$ Pore-Size Distribution $V_1(R)$, $\alpha = 1.0 \times 10^{-2}$

2 $\equiv$ Pore-Size Distribution $V_2(R)$, $\alpha = 1.0 \times 10^{-2}$

3 $\equiv$ Pore-Size Distribution $V_1(R)$, $\alpha = 2.0 \times 10^{-4}$

4 $\equiv$ Pore-Size Distribution $V_2(R)$, $\alpha = 2.0 \times 10^{-4}$

5 $\equiv$ Pore-Size Distribution $V_1(R)$, $\alpha = 1.0 \times 10^{-8}$

6 $\equiv$ Pore-Size Distribution $V_2(R)$, $\alpha = 1.0 \times 10^{-8}$

Figure 4. The Effect of Pressure on the Slip-Flow Correction Factors.

1 $\equiv$ ϕ_{SA} for Pore-Size Distribution $V_1(R)$

2 $\equiv$ ϕ_{SB} for Pore-Size Distribution $V_1(R)$

3 $\equiv$ ϕ_{SA} for Pore-Size Distribution $V_2(R)$

4 $\equiv$ ϕ_{SB} for Pore-Size Distribution $V_2(R)$

Figure 5. The Effect of Pressure on the Slip-Flow Correction Factors.

1 $\equiv$ ϕ_{SA} for Pore-Size Distribution $V_1(R)$

2 $\equiv$ ϕ_{SB} for Pore-Size Distribution $V_1(R)$

3 $\equiv$ ϕ_{SA} for Pore-Size Distribution $V_2(R)$

4 $\equiv$ ϕ_{SB} for Pore-Size Distribution $V_2(R)$

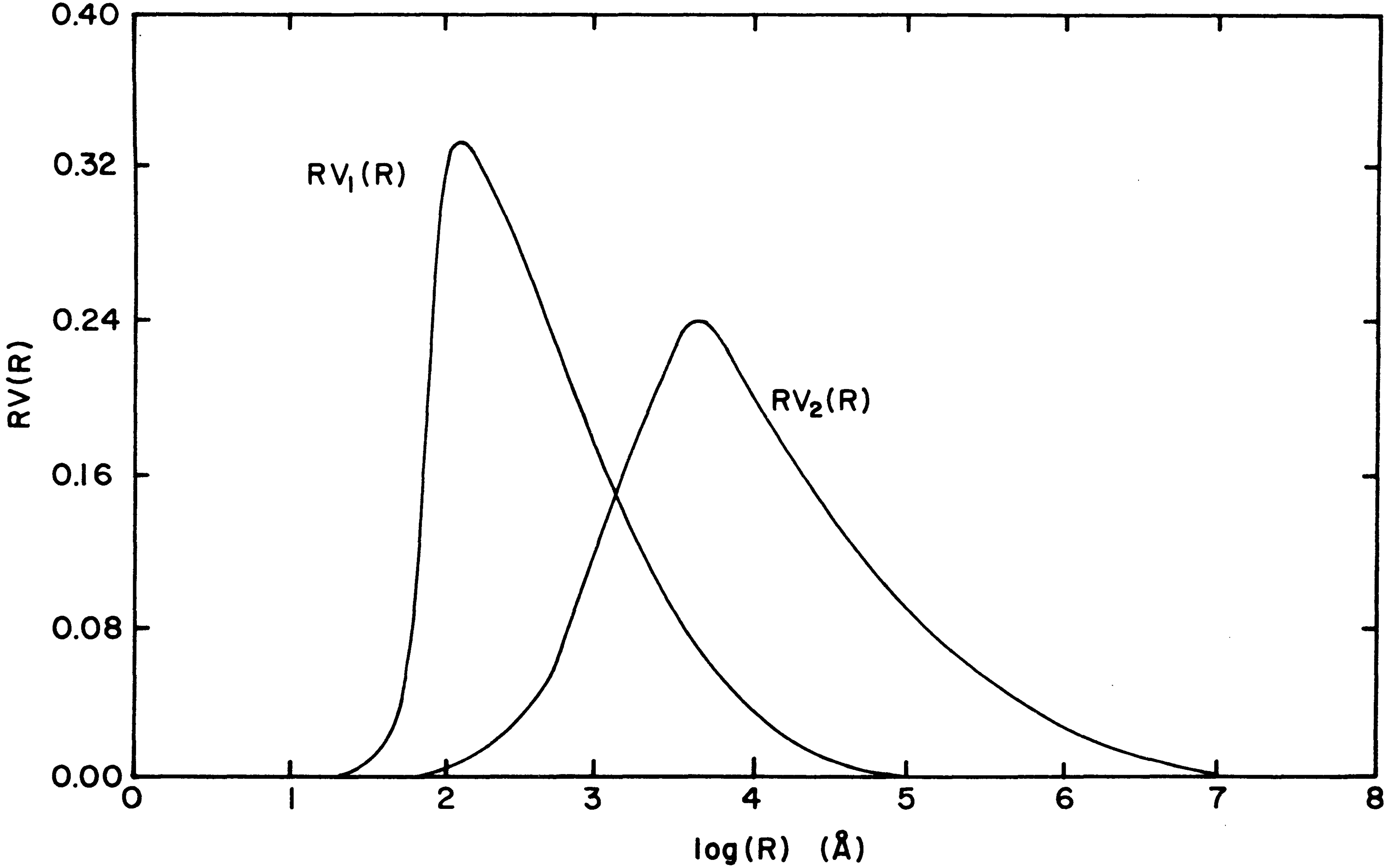


Figure 1.

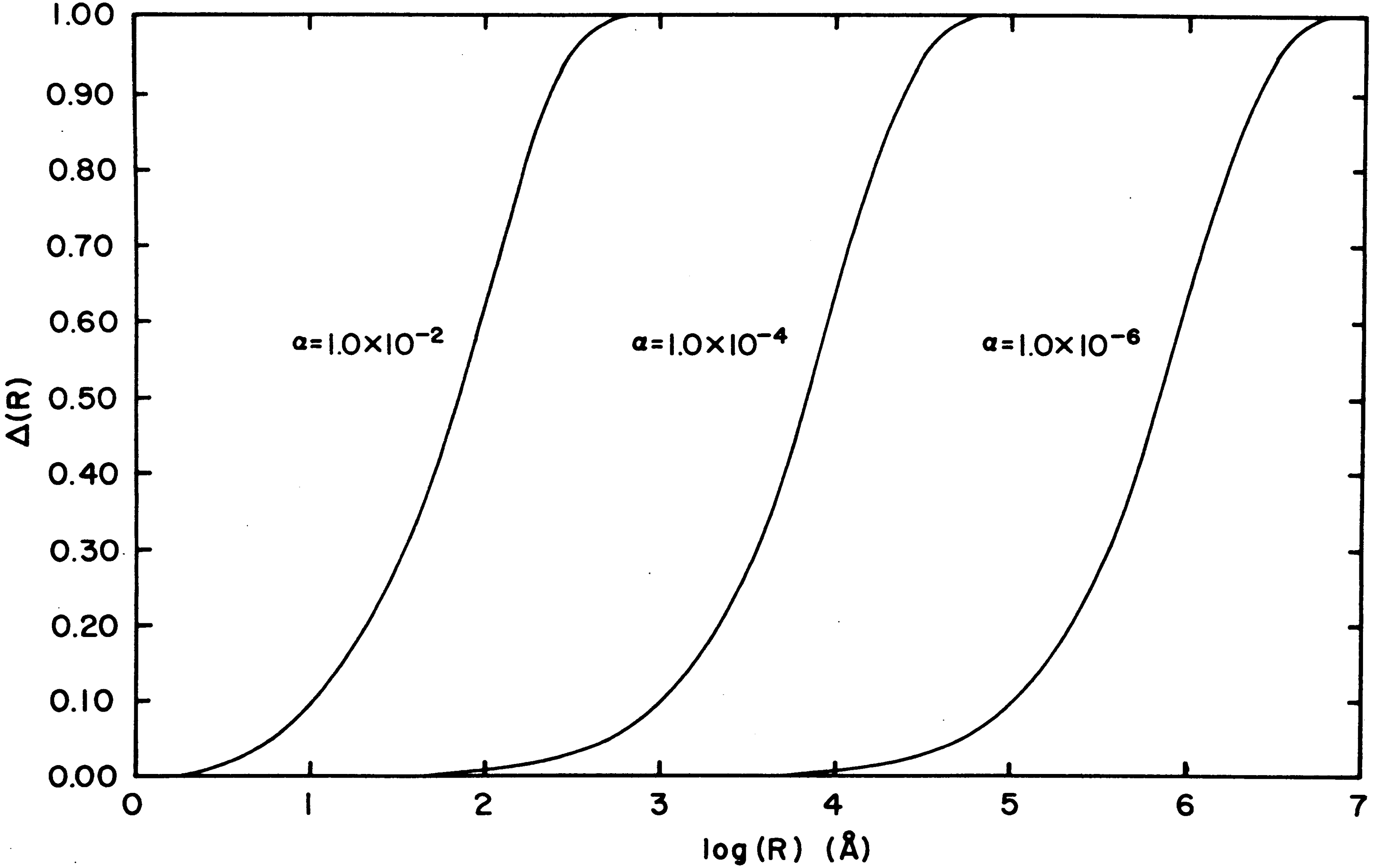
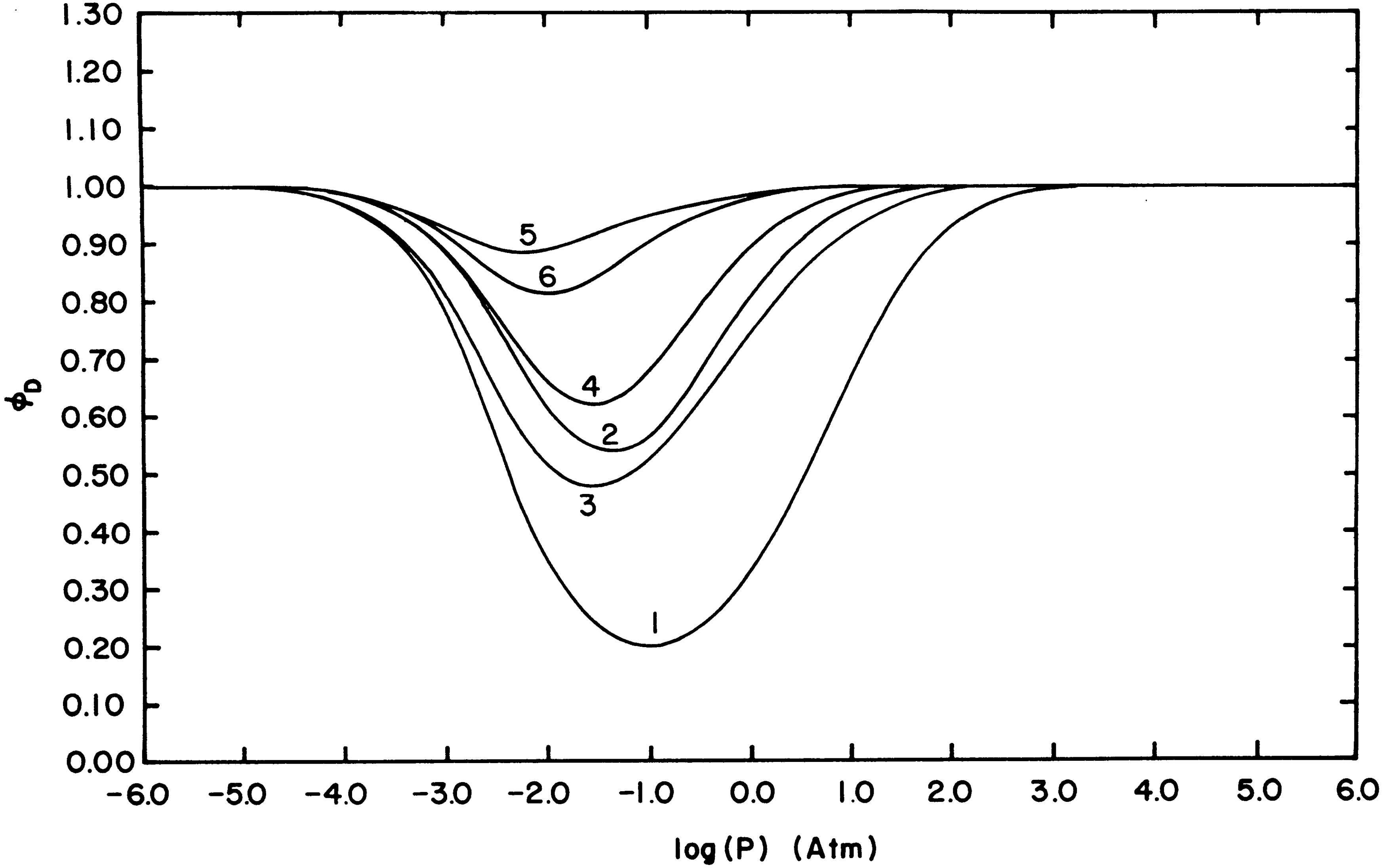

1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Δ(R)
0
1
2
3
4
5
6
7
log(R) (Å)
α=1.0×10⁻²
α=1.0×10⁻⁴
α=1.0×10⁻⁶

Figure 2.



1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
ϕ_D
5
6
4
2
3
1
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
log(P) (Atm)

Figure 3.

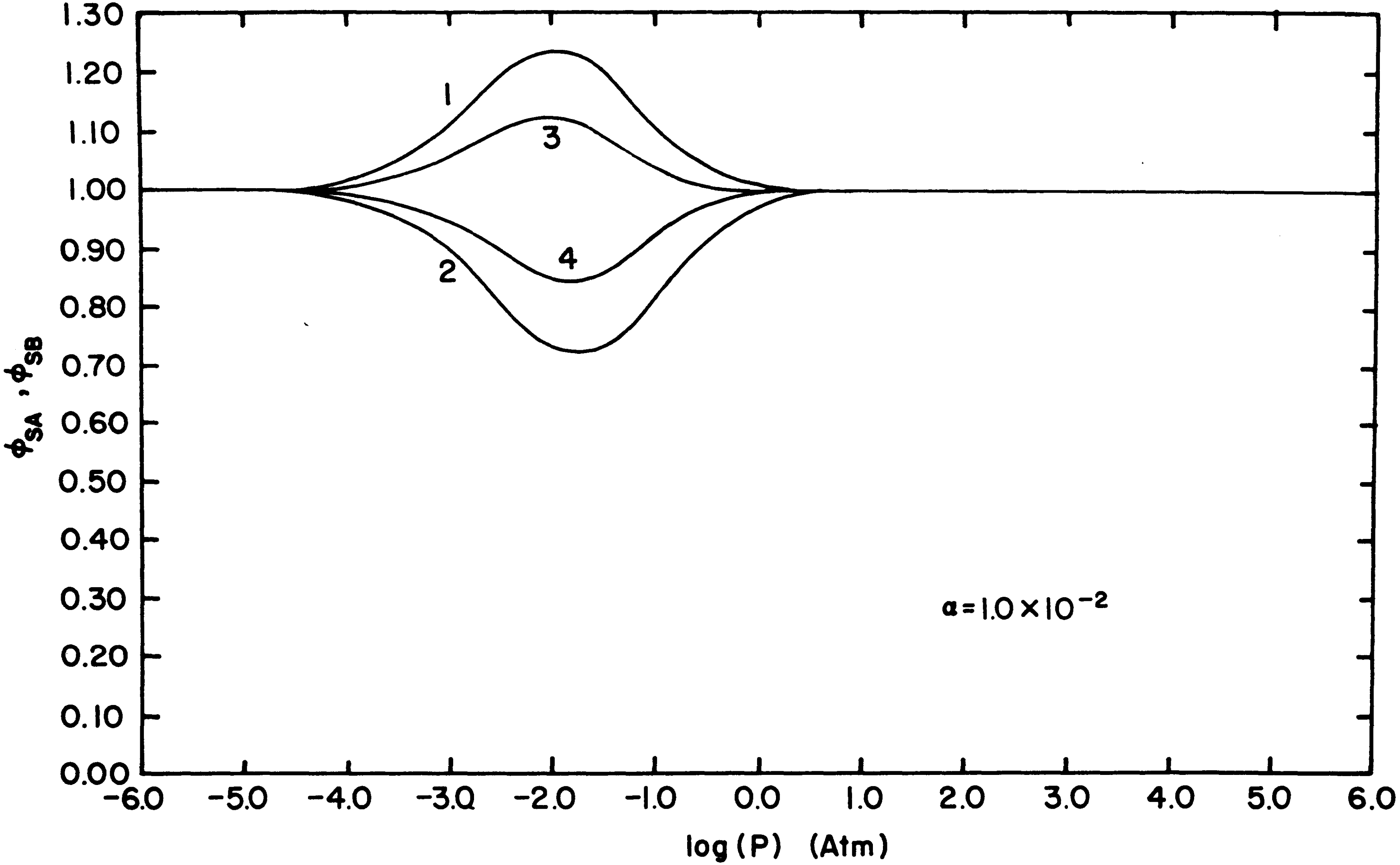

1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
ϕ_{SA}, ϕ_{SB}
1
3
4
2
$\alpha = 1.0 \times 10^{-2}$
−6.0
−5.0
−4.0
−3.0
−2.0
−1.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
log (P) (Atm)

Figure 4.

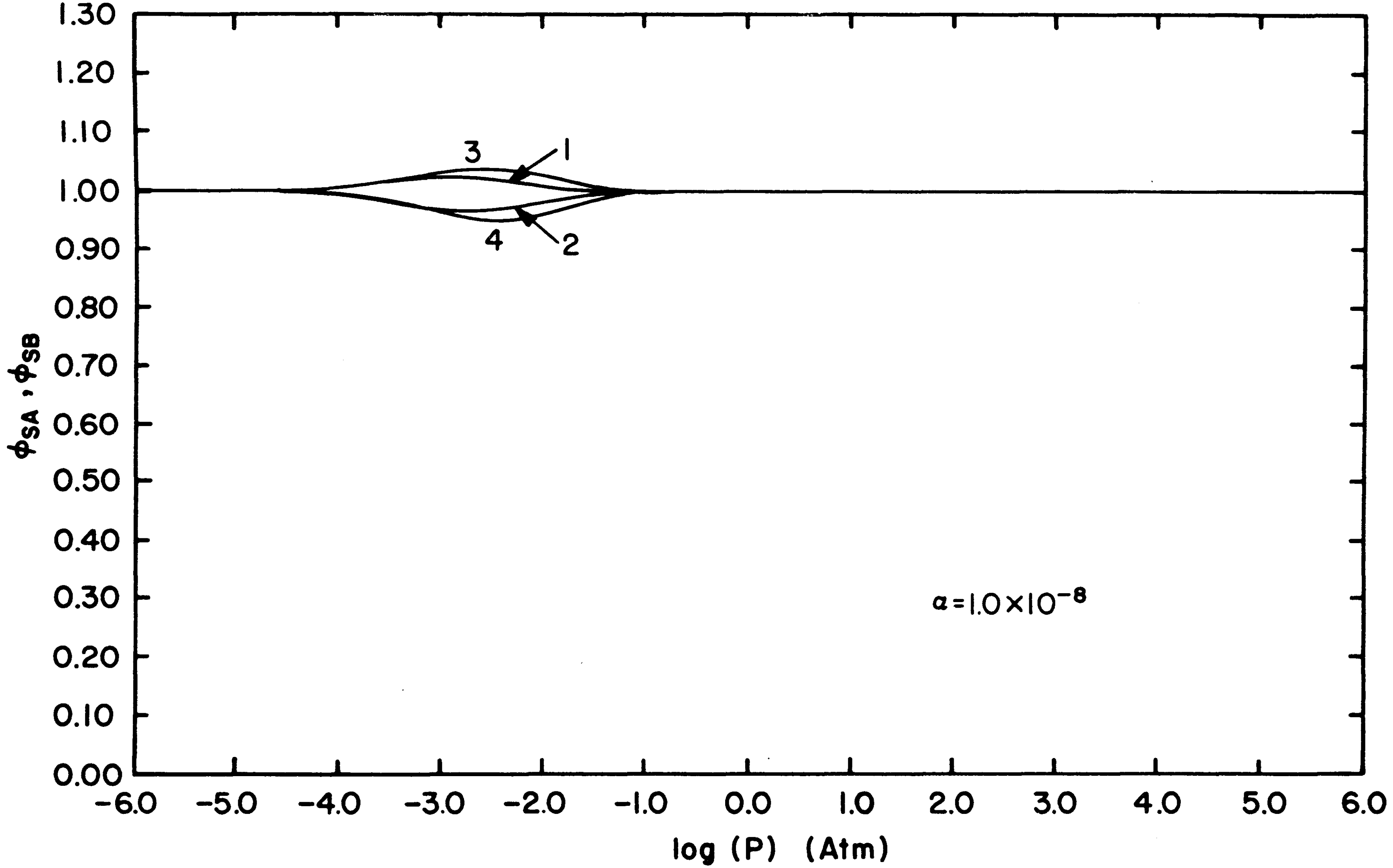

1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
ϕ_{SA}, ϕ_{SB}
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
log (P) (Atm)
3
1
4
2
$\alpha = 1.0 \times 10^{-8}$

Figure 5.

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CHEMICAL REACTIONS WITH MOLE CHANGES IN HETEROPOROUS CATALYSTS - PART I

by

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ABSTRACT

The modified dusty-gas model [1] is used to describe the mass fluxes for zero and first order irreversible reactions with mole changes in heteroporous catalysts, and to estimate their effectiveness factors in the transition regime. It is shown that the effectiveness factors predicted by the dusty-gas model (homoporous model) are larger than those calculated by the modified dusty-gas model (heteroporous model), in some cases by about 30%. In the Knudsen and molecular regimes, the correction factors of the modified dusty-gas model approach unity and the two models predict the same values for the effectiveness factors.

Since many industrial catalysts are heteroporous and operate in the transition region of transport, the transport equations and calculational procedures presented in this work are relevant to reactor design.

INTRODUCTION

Many industrial catalysts operate in the transition region of transport [2,3] and usually contain a random and tortuous arrangement of pores which may vary in size from several microns down to a few angstroms within the same particle. The effects of intraparticle transport on the kinetics of reaction in porous catalysts have been described in terms of the effectiveness factor concept [2,3]. Abed and Rinker [3] were the first to study the effectiveness factor behavior in the transition region of transport, and used in their studies the dusty-gas model to describe the transport for a zero-order, irreversible reaction with mole changes.

The dusty-gas model has been developed [4-6] to describe mass transfer in homoporous media and while it has a firmer theoretical basis than other current models [7], it fails to account for the effect of the nonuniformity of the porous structures of commercial catalysts. Deviations between experimental fluxes and those computed through the use of the dusty-gas model have been observed [8-10]. Klavetter, et al. [1] have modified the dusty-gas model through the use of correction factors which account for the effects the pore-size and tortuosity distributions have on the mass fluxes in heteroporous media. When the correction factors approach unity, the modified dusty-gas model approaches the behavior of the dusty gas equations; this occurs when the pressure of the system is either very low or very high because, at either extreme, almost all pores in a porous medium are in a single transport regime, that is either Knudsen or molecular diffusion. In their study, a comparison of the mass fluxes predicted by the modified dusty-gas and the dusty-gas models in the transition region of transport shows that the percentage deviation for binary systems may be, in some cases, significant (up to 75% for the porous media of their studies).

The work reported here presents the theoretical results for the effectiveness factors and mass fluxes of zero and first order irreversible reactions with mole changes occurring in two different heteroporous media. The modified dusty-gas model developed by Klavetter et al. [1] is used to describe the transport processes within the heteroporous catalyst pellets.

MATHEMATICAL FORMULATION

The mass transport equations of the modified dusty-gas model [1] for the system shown in Figure 1, when one-dimensional diffusion and flow occur in the porous medium, have the following form:

$$N_A = -a \frac{dy_A}{dz} - b \frac{dP}{dz} \tag{1}$$

$$N_B = - a' \frac{dy_B}{dz} - b' \frac{dP}{dz} \tag{2}$$

where

$$a = \frac{\phi_D C_2 D^o{}_{AB} K_A P}{(C_2 D^o{}_{AB} + K_m P) R_g T} \tag{3}$$

$$a' = \frac{\phi_D C_2 D^o_{AB} K_B P}{(C_2 D^o_{AB} + K_m P) R_g T} \tag{4}$$

$$b = [\frac{\phi_{SA} K_A (C_2 D^o_{AB} + K_B P)}{C_2 D^o_{AB} + K_m P} + \frac{C_o P}{\mu_m}] \frac{y_A}{R_g T} \tag{5}$$

$$b' = [\frac{\phi_{SB} K_B (C_2 D^o_{AB} + K_A P)}{C_2 D^o_{AB} + K_m P} + \frac{C_o P}{\mu_m}] \frac{y_B}{R_g T} \tag{6}$$

A steady-state molar balance for an irreversible reaction of nth order occurring in the porous slab of Figure 1, gives:

$$\frac{dN_A}{dz} = -k \left(\frac{y_A P}{R_g T}\right)^n \tag{7}$$

$$\frac{dN_B}{dz} = \theta k \left(\frac{y_A P}{R_g T}\right)^n \tag{8}$$

where the irreversible reaction has the form

$$A \rightarrow \theta B$$

In equations (7-8) ideal gas behavior has been assumed since the pressure range considered in this work will not introduce significant deviations from ideal behavior. For systems operating at fairly high pressures fugacities may be used.

The substitution of equations (1) and (2) into equations (7) and (8) yields the following expressions,

$$a\frac{d^2y_A}{dz^2} + \alpha_1\left(\frac{dy_A}{dz}\right)^2 + (\alpha_2 + \alpha_3)\left(\frac{dy_A}{dz}\right)\left(\frac{dP}{dz}\right) + \alpha_4\left(\frac{dP}{dz}\right)^2 + b\frac{d^2P}{dz^2} = k\left(\frac{y_AP}{R_gT}\right)^n \tag{9}$$

$$a'\frac{d^2y_A}{dz^2} + g\alpha_1\left(\frac{dy_A}{dz}\right)^2 + (g\alpha_2 - \alpha_5)\left(\frac{dy_A}{dz}\right)\left(\frac{dP}{dz}\right) - \alpha_6\left(\frac{dP}{dz}\right)^2 - b'\frac{d^2P}{dz^2} = \theta k\left(\frac{y_AP}{R_gT}\right)^n \tag{10}$$

where

$$g = \left(\frac{M_A}{M_B}\right)^{1/2},\ \alpha_1 = \frac{\partial a}{\partial y_A},\ \alpha_2 = \frac{\partial a}{\partial P},\ \alpha_3 = \frac{\partial b}{\partial y_A},\ \alpha_4 = \frac{\partial b}{\partial P},\ \alpha_5 = \frac{\partial b'}{\partial y_A},\ \alpha_6 = \frac{\partial b'}{\partial P} \tag{11}$$

The following boundary conditions are used for equations (9) and (10),

$$\text{at } z = 0,\ y_A = 1 \quad\text{and}\quad P = 1.01 \times 10^6 \tag{12}$$

$$\text{at } z = z_o,\ \frac{dy_A}{dz} = 0 \quad\text{and}\quad \frac{dP}{dz} = 0 \tag{13}$$

The above set of nonlinear ordinary differential equations is integrated through the use of the orthogonal collocation [11] method after making the space variable dimensionless by letting,

$$w = (z/L)/(z_o/L) = \frac{z}{LX_o} \tag{14}$$

where $X_o = z_o/L$, and the length z_o is the position within the slab at which the concentration of component A is equal to zero. The application of orthogonal collocation yields the following set of nonlinear algebraic equations,

$$\begin{aligned} & a \sum_{j=1}^{N+2} B_{ij}y_{Aj} + \alpha_1[\sum_{j=1}^{N+2} A_{ij}y_{Aj}]^2 \\ & + (\alpha_2 + \alpha_3)(\sum_{j=1}^{N+2} A_{ij}y_{Aj})(\sum_{j=1}^{N+2} A_{ij}P_j) + \alpha_4[\sum_{j=1}^{N+2} A_{ij}P_j]^2 \\ & + b \sum_{j=1}^{N+2} B_{ij}P_j = L^2X_o^2k\, (\frac{Y_{Ai}P_i}{R_gT})^n , \quad i = 2,3,\ldots, N+1 \end{aligned} \tag{15}$$

$$\begin{aligned} & a' \sum_{j=1}^{N+2} B_{ij}y_{Aj} + g\alpha_1[\sum_{j=1}^{N+2} A_{ij}y_{Aj}]^2 \\ & + (g\alpha_2 - \alpha_5)(\sum_{j=1}^{N+2} A_{ij}y_{Aj})(\sum_{j=1}^{N+2} A_{ij}P_j) - \alpha_6[\sum_{j=1}^{N+2} A_{ij}P_j]^2 \\ & - b' \sum_{j=1}^{N+2} B_{ij}P_j = L^2X_o^2\theta k\, (\frac{y_{Ai}P_i}{R_gT})^n , \quad i = 2,3,\ldots,N+1 \end{aligned} \tag{16}$$

The external collocation points i=1 and i=N+2 are taken to correspond at w=0 and w=1, and the following expressions for y_{A1}, P_1, $y_{A,N+2}$ and P_{N+2} are obtained through the use of the boundary conditions, equations (12) and (13):

$$y_{A1} = 1,\ P_1 = 1.01 \times 10^6 \tag{17}$$

$$\begin{aligned} y_{A,N+2} &= \frac{-[A_{N+2,1} + \sum_{j=2}^{N+1} A_{N+2,j} y_{Aj}]}{A_{N+2,N+2}}, \\ P_{N+2} &= \frac{-[A_{N+2,1} + \sum_{j=2}^{N+1} A_{N+2,j} P_j]}{A_{N+2,N=2}} \end{aligned} \tag{18}$$

By using equations (17) and (18) the variables y_{A1}, P_1, $y_{A,N+2}$ and P_{N+2} are eliminated from equations (15) and (16). Twelve internal collocation points (N=12) were used for the zero and first order reactions considered in this work, since N=12 proved to be sufficient to obtain differences in only the seventh digit in the predictions of y_A and P as compared to the higher approximation. Jacobi orthogonal polynomials were used in all computations.

The twenty four nonlinear algebraic equations were solved simultaneously through the use of a quadratically convergent Newton-like method based upon Gaussian elimination [12]. The effectiveness factor, η, is calculated as follows:

$$\eta = \frac{\frac{1}{V_P} \int_o^{V_p} r_A(C_A) dV}{r_A(C_A)\Big|_{z=0}} = \frac{\frac{1}{SL} \int_o^{1} r_A(C_A) SLX_o dw}{-k(\frac{y_A P}{R_g T})^n\Big|_{w=0}} \tag{19}$$

where

$$r_A(C_A) = -kC_A^n = -k(\frac{y_A P}{R_g T})^n \tag{20}$$

RESULTS

The dusty-gas model ($\phi_D = \phi_{SA} = \phi_{SB} = 1.0$) is used in determining through an iterative process, the length X at which $y \cong 0$ for a given rate constant k of a reaction rate. Another approach is to set the value of X_o and then find the rate constant k which makes $y_A\Big|_{X_o} \cong 0$, when the dusty-gas model is used. The latter procedure was used in the calculation of the results of the present work. Then, these values of the rate constants are used in the modified dusty-gas model and through an iterative process the value of X_o is obtained at which $y_A \cong 0$. The effectiveness factors may now be estimated by the predictions of the two models and comparisons can be made.

Zero and first order reactions were examined in this study and the values of the model parameters are: $C_0 = 5.0 \times 10^{-10}$, $C_1 = 1.0 \times 10^{-5}$, $C_2 = 0.5$, $L = 1.0$, and $T = 299.3°K$. Two different pore-size distributions, $V_1(R)$ and $V_2(R)$ were used in the calculations, and their diagrams are given in Figure 1 of Reference [1].

In Tables 1 and 2, the values of the effectiveness factors for $\theta = 3$ are presented. The largest deviations in the effectiveness factors predicted by the dusty-gas and the modified dusty-gas models occur when $\alpha = 10^{-2}$ for both pore-size distributions. The results show that there is a substantial decline in the deviation as α changes values from 10^{-2} to 10^{-4} because the values of ϕ_D rapidly approach unity at the smaller value of α at this operating pressure. The values of ϕ_D for $\alpha = 10^{-6}$, 10^{-8}, and 10^{-10} are very close to unity at the operating pressure, and thus, the deviation is small. Likewise, the deviations from unity of the values of ϕ_D for the $V_1(R)$ distribution were found to be greater than those of the distribution $V_2(R)$, and this explains the differences in the deviations of the effectiveness factors calculated for the two distributions. The effect of ϕ_{SA} and ϕ_{SB} on the observed deviations is very small, since their values differ from unity by an insignificant amount even when $\alpha = 10^{-2}$. It should also be noted that while the magnitude of η is lower for the first order reaction, the percentage deviations in the effectiveness factors of the first and zero order reactions are approximately the same.

In Tables 3 and 4 the values of the effectiveness factors for $\theta = 2$ are presented, and in Tables 5 and 6 the values of η for $\theta = 1/2$

are shown. The observations and comments made in the above paragraph are also appropriate for the data in Tables 3-6. It is seen from Tables 1-6, that changes in the value of θ have only a minor effect on the deviations of the effectiveness factors.

In Figures 2 and 3 the mass flux of component A versus the length z/L is plotted for the zero-order reaction and for both $V_1(R)$ and $V_2(R)$. It is clear that the dusty-gas model predicts larger fluxes and therefore effectiveness factors than those computed by the modified dusty-gas model, especially for the $V_1(R)$ distribution. The mass fluxes of component A shown in Figures 4 and 5 vary with respect to z/L in a nonlinear fashion, as should be the case for reaction orders $n > 1$. Also, for the first order reaction the modified dusty-gas model predicts fluxes of lower magnitude than those calculated by the dusty-gas model, and the difference is larger in the case of the $V_1(R)$ distribution. Similar results as those shown in Figures 2-5 were obtained for $\theta = 1/2$ and $\theta = 3$ [13].

Detailed calculations [13] have shown that as θ decreases the concentration profile of component A becomes less steep and the pressure gradient decreases, while the mass flux of A increases as does the reaction rate, r_A.

CONCLUSIONS AND REMARKS

The results of this work show that the effectiveness factors in the transition region, estimated by the modified dusty-gas model are smaller (up to about 30% for the systems examined) than those predicted by the dusty-gas model which does not account for the effects the pore-size and tortuosity distributions have on the mass fluxes in industrial heteroporous catalysts. In the Knudsen and molecular regimes, on each side of the transition region, the correction factors of the modified dusty-gas model approach unity and the two models predict the same values for the effectiveness factors.

Since the modified dusty-gas model is applicable to heteroporous media, its use in describing mass transport in porous catalysts would allow the reactor designer to obtain correct effectiveness factors over the entire range of transport regimes.

ACKNOWLEDGMENT

The authors express their appreciation to the Weldon Springs Fund of the University of Missouri for support of this work.

NOTATION

A_{ij} ≡ elements of the discretization matrix of the differential operators $\frac{\partial y_A}{\partial z}$ and $\frac{\partial P}{\partial z}$

B_{ij} ≡ elements of the discretization matrix of the differential operators $\frac{\partial^2 y_A}{\partial z^2}$ and $\frac{\partial^2 P}{\partial z^2}$

C_A ≡ concentration of component A, g-moles/cm^3

C_0 ≡ constant dependent only upon structure of porous medium and giving relative D'Arcy flow permeability, cm^2

C_1 ≡ constant dependent only upon structure of porous medium and giving relative Knudsen flow permeability, cm

C_2 ≡ constant dependent only upon structure of porous medium and giving ratio of molecular diffusivity within the porous medium to the free gas diffusivity, dimensionless

D_{AB} ≡ free gas mutual diffusivity in a binary mixture of A and B, cm^2/sec

D°_{AB} ≡ $D_{AB}P$

k ≡ reaction constant

K_A ≡ $C_1(R_gT/M_A)^{1/2}$, effective Knudsen diffusivity of A, cm^2/sec

K_B ≡ $C_1(R_gT/M_B)^{1/2}$, effective Knudsen diffusivity of B, cm^2/sec

K_m ≡ $y_AK_B + y_BK_A$, effective Knudsen diffusivity of the gas mixture, cm^2/sec

L ≡ length of catalyst pellet, cm

M_A ≡ molecular weight of A, g/g-mole

M_B ≡ molecular weight of B, g/g-mole

n ≡ order of the reaction

N ≡ number of internal collocation points

N_A ≡ molar flux of A, g-moles/cm^2-sec

N_B ≡ molar flux of B, g-moles/cm^2-sec

P ≡ total pressure, dyn/cm^2

r_A ≡ reaction rate of component A

R ≡ pore radius, Å

R_g ≡ gas constant, 8.317 x 10^7 erg/g-mole-°K

T ≡ absolute temperature, °K

V_P ≡ volume of catalyst pellet, cm^3

$V_1(R)$ ≡ volume percent of pores with radius, R, in porous medium 1, dimensionless

$V_2(R)$ ≡ volume percent of pores with radius, R, in porous medium 2, dimensionless

w ≡ z/LX_0, dimensionless length

X_0 ≡ z_0/L, dimensionless length at which $y_A = 0$

y_A ≡ mole fraction of component A, dimensionless

y_B ≡ mole fraction of component B, dimensionless

z ≡ distance in the direction of mass transfer, cm

z_0 ≡ distance in the pellet at which $y_A = 0$

GREEK SYMBOLS

α ≡ characteristic parameter of the function $\Delta(R)$ of Reference [1], $\mathring{A}^{-1}$

η ≡ effectiveness factor defined by equation (19), dimensionless

θ ≡ number of moles of B produced by one mole of A

μ_m ≡ viscosity of the mixture of species A and B, g/cm-sec

ϕ_D ≡ diffusion-flow correction factor (Reference [1]), dimensionless

ϕ_{SA} ≡ slip-flow correction factor (Reference [1]), dimensionless

ϕ_{SB} ≡ slip-flow correction factor (Reference [1]), dimensionless

SUBSCRIPTS

DG ≡ dusty-gas model

MDG ≡ modified dusty-gas model

TABLE HEADINGS

Table 1. Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_1(R)$ Pore-Size Distribution and for $\theta=3$.

Table 2. Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_2(R)$ Pore-Size Distribution and for $\theta=3$.

Table 3. Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_1(R)$ Pore-Size Distribution and for $\theta=2$.

Table 4. Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_2(R)$ Pore-Size Distribution and for $\theta=2$.

Table 5. Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_1(R)$ Pore-Size Distribution and for $\theta=1/2$.

Table 6. Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_2(R)$ Pore-Size Distribution and for $\theta=1/2$.

TABLE 1

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_1(R)$ Pore-Size Distribution and for $\theta=3$.

	ZERO-ORDER REACTION				FIRST-ORDER REACTION			
	$k(\frac{\text{g moles}}{\text{cm}^3\ \text{sec}})$	η_{DG}	η_{MDG}	% DEV	$k\ (\text{sec}^{-1})$	η_{DG}	η_{MDG}	% DEV
$\phi_D = \phi_{SA} = \phi_{SB} = 1.0$ (Dusty-Gas Model)	3.116×10^{-6}	0.90	-	-	1.526	0.1306	-	-
$\alpha = 10^{-2}$	3.116×10^{-6}	0.90	0.6389	29.0	1.526	0.1306	0.0926	29.1
$\alpha = 10^{-4}$	3.116×10^{-6}	0.90	0.8443	6.2	1.526	0.1306	0.1225	6.2
$\alpha = 10^{-6}$	3.116×10^{-6}	0.90	0.8921	0.9	1.526	0.1306	0.1294	0.9
$\alpha = 10^{-8}$	3.116×10^{-6}	0.90	0.8931	0.8	1.526	0.1306	0.1296	0.8
$\alpha = 10^{-10}$	3.116×10^{-6}	0.90	0.8931	0.8	1.526	0.1306	0.1296	0.8

$$\%\ \text{DEV} = \frac{\eta_{DG} - \eta_{MDG}}{\eta_{DG}} \times 100$$

TABLE 2

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_2(R)$ Pore-Size Distribution and for $\theta=3$.

	ZERO-ORDER REACTION				FIRST-ORDER REACTION			
	$k(\frac{g\ moles}{cm^3\ sec})$	η_{DG}	η_{MDG}	% DEV	$k\ (sec^{-1})$	η_{DG}	η_{MDG}	% DEV
$\phi_D = \phi_{SA} = \phi_{SB} = 1.0$ (Dusty-Gas Model)	3.116×10^{-6}	0.90	-	-	1.526	0.1306	-	-
$\alpha = 10^{-2}$	3.116×10^{-6}	0.90	0.8573	4.7	1.526	0.1306	0.1243	4.8
$\alpha = 10^{-4}$	3.116×10^{-6}	0.90	0.8845	1.7	1.526	0.1306	0.1283	1.8
$\alpha = 10^{-6}$	3.116×10^{-6}	0.90	0.8958	0.5	1.526	0.1306	0.1300	0.5
$\alpha = 10^{-8}$	3.116×10^{-6}	0.90	0.8961	0.4	1.526	0.1306	0.1300	0.5
$\alpha = 10^{-10}$	3.116×10^{-6}	0.90	0.8961	0.4	1.526	0.1306	0.1300	0.5

$$\%\ DEV = \frac{\eta_{DG} - \eta_{MDG}}{DG} \times 100$$

TABLE 3

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_1(R)$ Pore-Size Distribution and for $\theta=2$.

	ZERO-ORDER REACTION				FIRST ORDER REACTION			
	$k(\frac{\text{g moles}}{\text{cm}^3\ \text{sec}})$	η_{DG}	η_{MDG}	% DEV	$k\ (\text{sec}^{-1})$	η_{DG}	η_{MDG}	% DEV
$\phi_D = \phi_{SA} = \phi_{SB} = 1.0$ (Dusty-Gas Model)	4.741×10^{-6}	0.90	-	-	2.097	0.1421	-	-
$\alpha = 10^{-2}$	4.741×10^{-6}	0.90	0.6276	30.3	2.097	0.1421	0.0990	30.3
$\alpha = 10^{-4}$	4.741×10^{-6}	0.90	0.8399	6.7	2.097	0.1421	0.1327	6.6
$\alpha = 10^{-6}$	4.741×10^{-6}	0.90	0.8908	1.0	2.097	0.1421	0.1407	1.0
$\alpha = 10^{-8}$	4.741×10^{-6}	0.90	0.8919	0.9	2.097	0.1421	0.1409	0.8
$\alpha = 10^{-10}$	4.741×10^{-6}	0.90	0.8919	0.9	2.097	0.1421	0.1409	0.8

$$\%\ \text{DEV} = \frac{\eta_{DG} - \eta_{MDG}}{\eta_{DG}} \times 100$$

TABLE 4

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_2(R)$ Pore-Size Distribution and for θ=2.

		ZERO-ORDER REACTION				FIRST-ORDER REACTION		
	$k(\frac{\text{g moles}}{\text{cm}^3\ \text{sec}})$	η_{DG}	η_{MDG}	% DEV	$k\ (\text{sec}^{-1})$	η_{DG}	η_{MDG}	% DEV
$\phi_D = \phi_{SA} = \phi_{SB} = 1.0$ (Dusty-Gas Model)	4.741×10^{-6}	0.90	-	-	2.097	0.1421	-	-
$\alpha = 10^{-2}$	4.741×10^{-6}	0.90	0.8527	5.3	2.097	0.1421	0.1347	5.2
$\alpha = 10^{-4}$	4.741×10^{-6}	0.90	0.8823	2.0	2.097	0.1421	0.1394	1.9
$\alpha = 10^{-6}$	4.741×10^{-6}	0.90	0.8946	0.6	2.097	0.1421	0.1413	0.6
$\alpha = 10^{-8}$	4.741×10^{-6}	0.90	0.8950	0.6	2.097	0.1421	0.1414	0.5
$\alpha = 10^{-10}$	4.741×10^{-6}	0.90	0.8950	0.6	2.097	0.1421	0.1414	0.5

$$\%\ \text{DEV} = \frac{\eta_{DG} - \eta_{MDG}}{\eta_{DG}} \times 100$$

TABLE 5

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_1(R)$ Pore-Size Distribution and for $\theta=1/2$.

	ZERO-ORDER REACTION				FIRST-ORDER REACTION			
	$k(\frac{\text{g moles}}{\text{cm}^3\ \text{sec}})$	η_{DG}	η_{MDG}	% DEV	$k\ (\text{sec}^{-1})$	η_{DG}	η_{MDG}	% DEV
$\phi_D = \phi_{SA} = \phi_{SB} = 1.0$ (Dusty-Gas Model)	9.461×10^{-6}	0.90	-	-	3.141	0.1817	-	-
$\alpha = 10^{-2}$	9.461×10^{-6}	0.90	0.6274	30.3	3.141	0.1817	0.1267	30.3
$\alpha = 10^{-4}$	9.461×10^{-6}	0.90	0.8403	6.6	3.141	0.1817	0.1697	6.6
$\alpha = 10^{-6}$	9.461×10^{-6}	0.90	0.8915	0.9	3.141	0.1817	0.1800	0.9
$\alpha = 10^{-8}$	9.461×10^{-6}	0.90	0.8925	0.8	3.141	0.1817	0.1802	0.8
$\alpha = 10^{-10}$	9.461×10^{-6}	0.90	0.8925	0.8	3.141	0.1817	0.1802	0.8

$$\%\ \text{DEV} = \frac{\eta_{DG} - \eta_{MDG}}{\eta_{DG}} \times 100$$

TABLE 6

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for the $V_2(R)$ Pore-Size Distribution and for $\theta=1/2$.

	ZERO-ORDER REACTION				FIRST-ORDER REACTION			
	$k(\frac{g\ moles}{cm^3\ sec})$	η_{DG}	η_{MDG}	% DEV	$k\ (sec^{-1})$	η_{DG}	η_{MDG}	% DEV
$\phi_D = \phi_{SA} = \phi_{SB} = 1.0$ (Dusty-Gas Model)	9.461×10^{-6}	0.90	-	-	3.141	0.1817	-	-
$\alpha = 10^{-2}$	9.461×10^{-6}	0.90	0.8352	5.2	3.141	0.1817	0.1722	5.2
$\alpha = 10^{-4}$	9.461×10^{-6}	0.90	0.8829	1.9	3.141	0.1817	0.1782	1.9
$\alpha = 10^{-6}$	9.461×10^{-6}	0.90	0.8953	0.5	3.141	0.1817	0.1807	0.6
$\alpha = 10^{-8}$	9.461×10^{-6}	0.90	0.8957	0.5	3.141	0.1817	0.1808	0.5
$\alpha = 10^{-10}$	9.461×10^{-6}	0.90	0.8957	0.5	3.141	0.1817	0.1808	0.5

$$\%\ DEV = \frac{\eta_{DG} - \eta_{MDG}}{\eta_{DG}} \times 100$$

FIGURE CAPTIONS

Figure 1. Mass Flux and Coordinate Directions in One-Dimensional Catalyst Pellet.

Figure 2. Mass Flux of Component A versus Pellet Length for the Zero Order Reaction with θ=2 and Pore-Size Distribution $V_1(R)$.

Figure 3. Mass Flux of Component A versus Pellet Length for the Zero Order Reaction with θ=2 and Pore-Size Distribution $V_2(R)$.

Figure 4. Mass Flux of Component A versus Pellet Length for the First Order Reaction with θ=2 and Pore-Size Distribution $V_1(R)$.

Figure 5. Mass Flux of Component A versus Pellet Length for the First Order Reaction with θ=2 and Pore-Size Distribution $V_2(R)$.

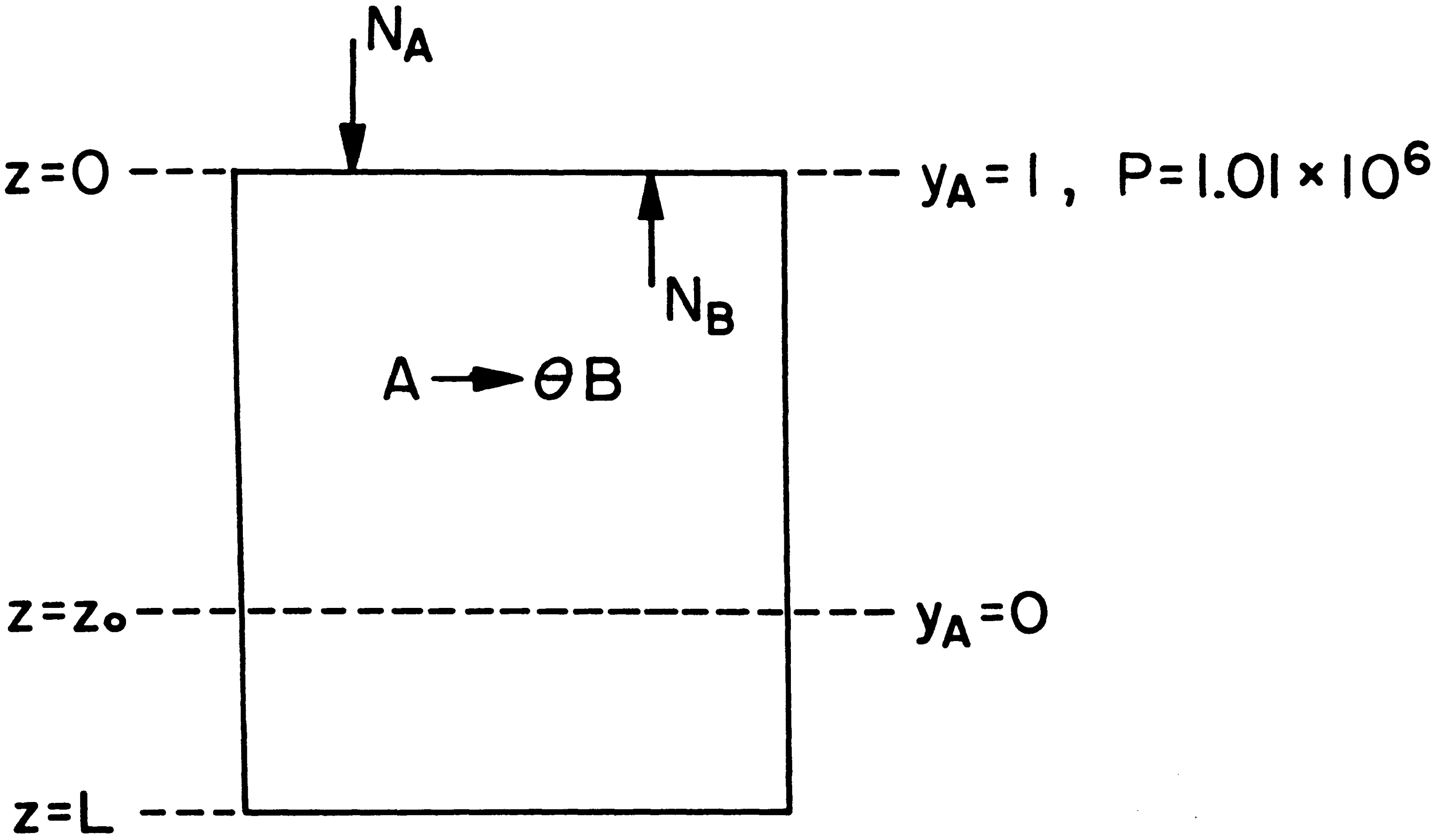

Figure 1.

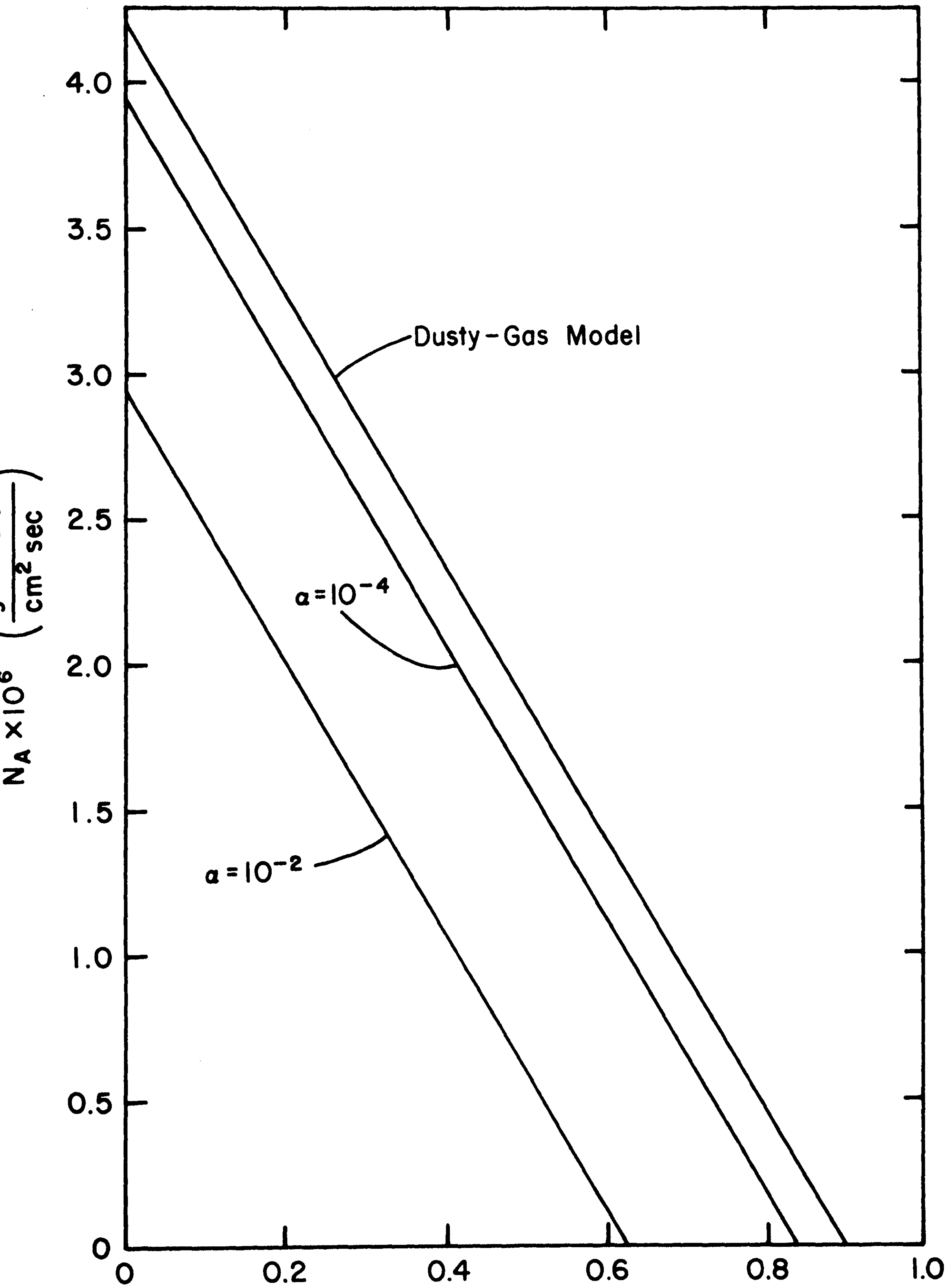
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
$N_A \times 10^6$ $\left(\frac{\text{gm moles}}{\text{cm}^2\,\text{sec}}\right)$
Dusty-Gas Model
$\alpha = 10^{-4}$
$\alpha = 10^{-2}$
0
0.2
0.4
0.6
0.8
1.0
z/L

Figure 2.

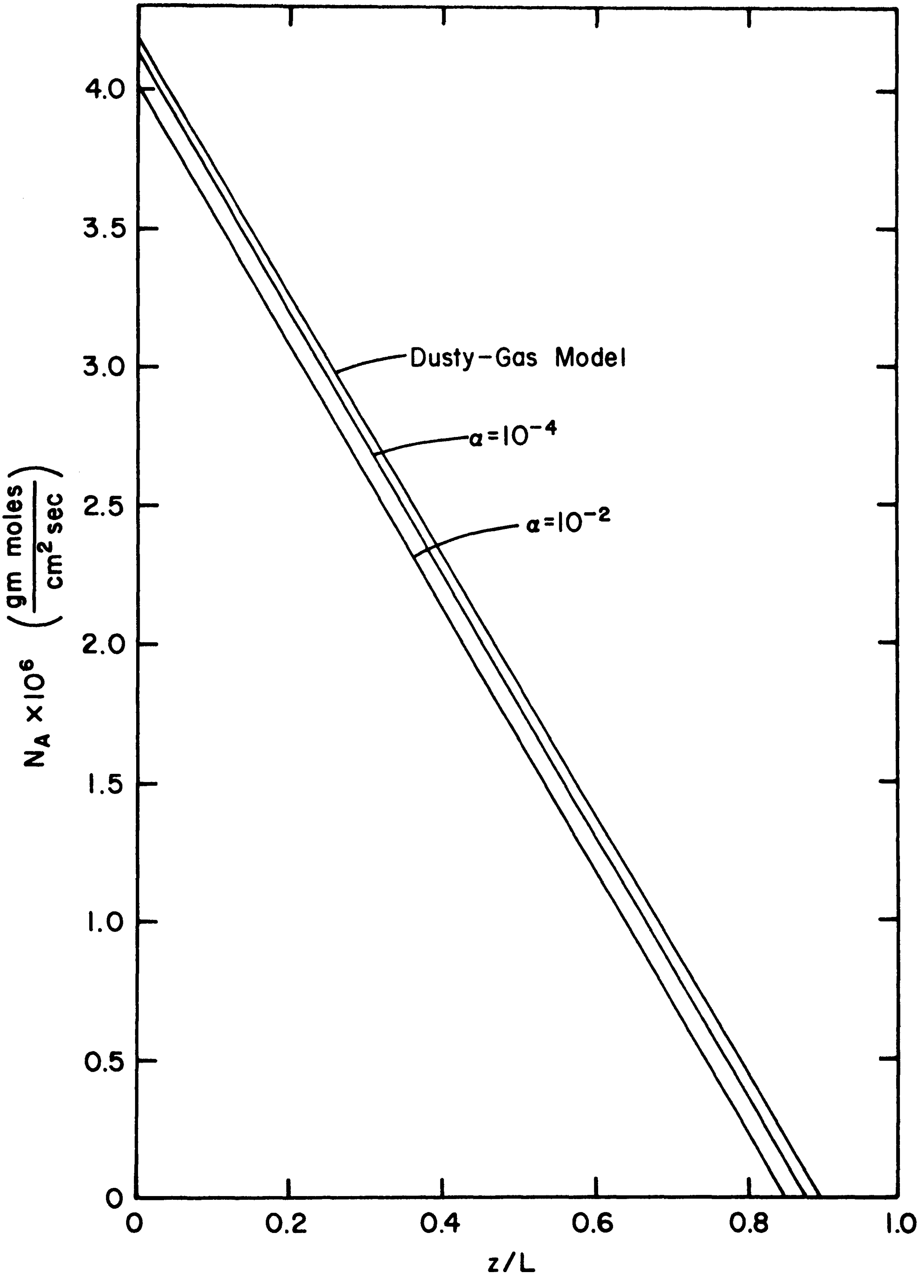
$N_A \times 10^6 \left(\frac{\text{gm moles}}{\text{cm}^2\text{sec}}\right)$
z/L
0
0.2
0.4
0.6
0.8
1.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Dusty-Gas Model
$\alpha=10^{-4}$
$\alpha=10^{-2}$

Figure 3.

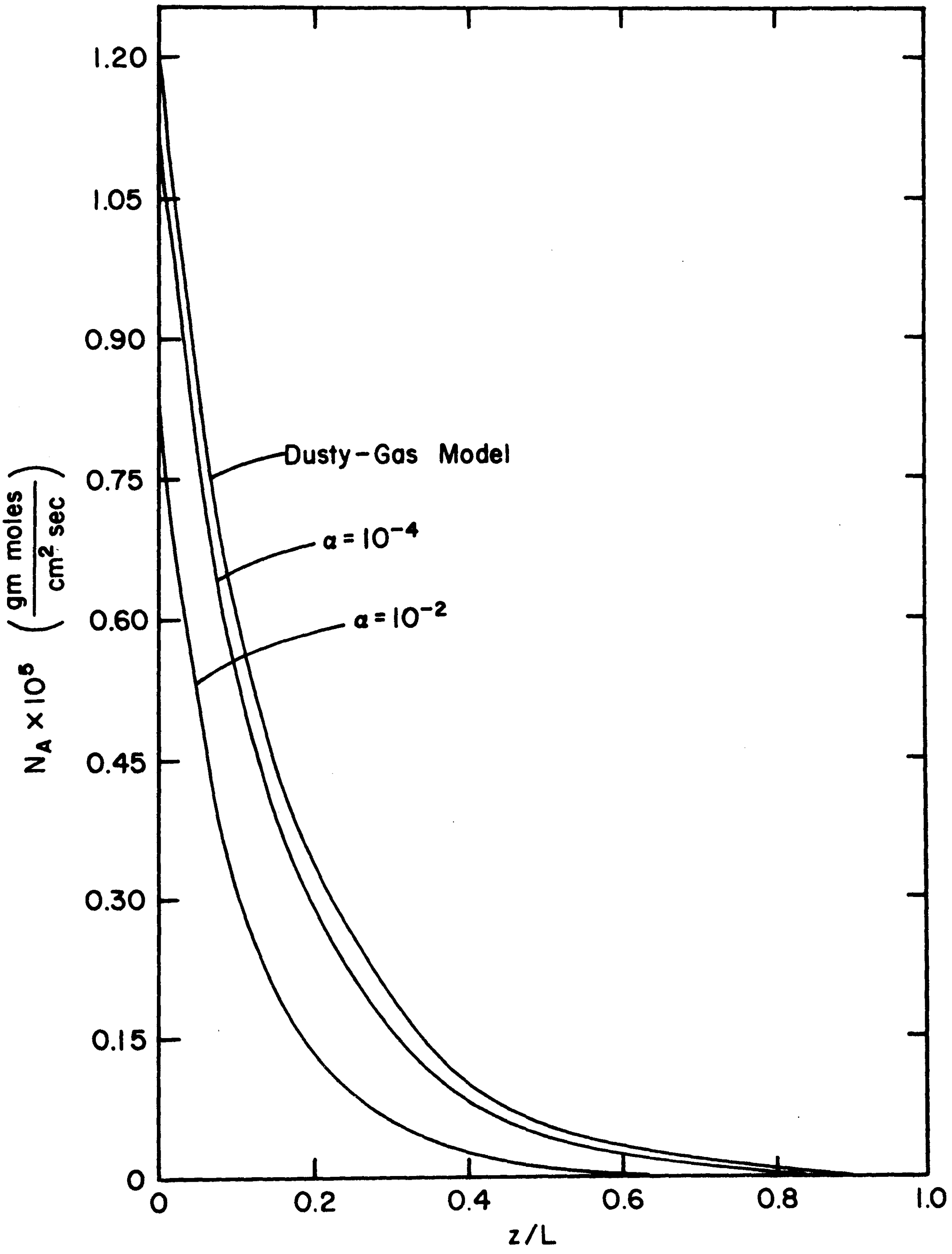
1.20
1.05
0.90
0.75
0.60
0.45
0.30
0.15
0
$N_A \times 10^5$ $\left(\frac{\text{gm moles}}{\text{cm}^2\ \text{sec}}\right)$
Dusty-Gas Model
$\alpha = 10^{-4}$
$\alpha = 10^{-2}$
0
0.2
0.4
0.6
0.8
1.0
z/L

Figure 4.

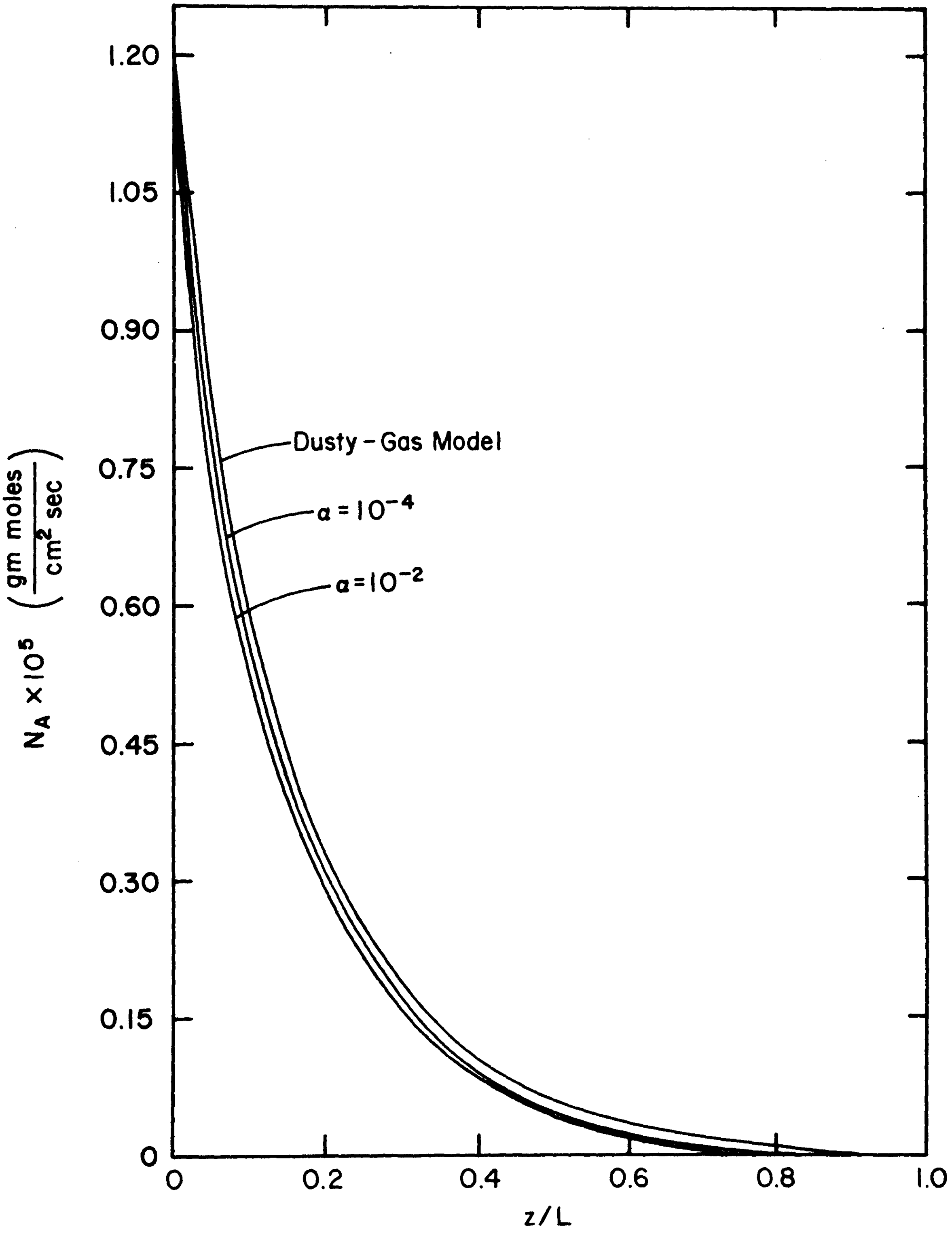
1.20
1.05
0.90
0.75
0.60
0.45
0.30
0.15
0
$N_A \times 10^5 \left(\frac{\text{gm moles}}{\text{cm}^2\ \text{sec}}\right)$
0
0.2
0.4
0.6
0.8
1.0
z/L
Dusty - Gas Model
$\alpha = 10^{-4}$
$\alpha = 10^{-2}$

Figure 5.

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CHEMICAL REACTIONS WITH MOLE CHANGES IN HETEROPOROUS CATALYSTS-PART II

by

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ABSTRACT

The modified dusty-gas model is used to describe the mass fluxes and estimate the effectiveness factors in the transition regime of second order irreversible reactions with mole changes in heteroporous catalysts. A comparison with the dusty-gas model shows that the dusty-gas model (homoporous model) predicts effectiveness factors that are larger than those predicted by the modified dusty-gas model, in some cases by about 30%. In the Knudsen and molecular regimes, the correction factors of the modified dusty-gas model approach unity and the two models predict the same results.

Since many industrial catalysts are heteroporous and operate in the transition region of transport, the transport equations used in this work are relevant to reactor design.

INTRODUCTION

In Part I [1] of this work the modified dusty-gas model [2] was used to describe the mass fluxes for zero and first order irreversible reactions with mole changes in heteroporous catalysts, and to estimate their effectiveness factors in the transition regime of transport. It was shown [1] that the effectiveness factors predicted by the dusty-gas model (homoporous model) [2,3] are larger than those calculated by the modified dusty-gas model (heteroporous model) [2], in some cases by about 30%.

In this note, the dusty-gas and the modified dusty-gas models are used to describe the mass fluxes and estimate the effectiveness factors in the transition regime, of second order irreversible reactions with mole changes in heteroporous catalysts. A comparison of the results obtained through the use of the above two models, is presented in this work.

MATHEMATICAL FORMULATION

The mass transport equations of the dusty-gas and modified dusty-gas models for the system shown in Figure 1, when one-dimensional diffusion and flow occur in a reactive porous medium, are given in Reference [1].

The effectiveness factor η is calculated as follows:

$$\eta = \frac{\frac{1}{V_P}\int_o^{V_p} r_A(C_A)dV}{r_A(C_A)\Big|_{z=0}} = \frac{\frac{1}{SL}\int_o^{1} r_A(C_A)SLX_o dw}{-k(\frac{y_A P}{R_g T})^n\Big|_{w=0}} \tag{1}$$

where

$$r_A(C_A) = -kC_A^n = -k(\frac{y_A P}{R_g T})^n \tag{2}$$

and n = 2 for a second order reaction. The solution procedure of the mathematical models and that of the determination of z_0 at which $y_A = 0$, are the same with those presented in [1]; the only difference is that n = 2 instead of 0 and 1 as it was the case in the study given in [1].

RESULTS

Second order reactions were examined in this study and the values of the model parameters are: $C_o = 5.0 \times 10^{-10}$, $C_1 = 1.0 \times 10^{-5}$, $C_2 = 0.5$, L = 1.0, and T = 299.3°K. Two different pore-size distributions, $V_1(R)$ and $V_2(R)$ were used in the calculations, and their diagrams are given in Figure 1 of Reference [2].

In Tables 1-3, the values of the effectiveness factors for $\theta = 3,2,1/2$ are presented. The largest deviations in the effectiveness factors predicted by the dusty-gas and the modified dusty-gas models occur when $\alpha = 10^{-2}$ for both pore-size distributions. The results show a substantial decline in the deviation as α changes values from 10^{-2} to 10^{-4}. This happens because the values of the diffusion-flow correction factor [2], for $\alpha = 10^{-6}$, 10^{-8}, and 10^{-10} are very close to unity at the operating pressure, and thus the deviation is small. Likewise, the deviations from unity of the values of the diffusion-flow correction factor for the $V_1(R)$ distribution were found to be greater than those of the distribution $V_2(R)$, and this explains the differences in the deviations of the effectiveness factors calculated for the two distributions. The effect of the slip-flow correction factors on the observed deviations is very small, since their values differ from unity by an insignificant amount [4] even when $\alpha = 10^{-2}$. It is also seen from Tables 1-3, that changes in the value of θ have only a minor effect in the deviations of the effectiveness factors.

In Figures 2 and 3 the mass flux of component A versus the length, z/L, is plotted, for $V_1(R)$ and $V_2(R)$, and for $\theta = 2$. It is clear that the dusty-gas model predicts larger fluxes and therefore effectiveness factors than those computed by the modified dusty-gas model, especially for the $V_1(R)$ distribution. Similar results were also obtained with $\theta = 1/2$ and $\theta = 3$ [4].

The variation of the values of the parameters C_0, C_1, and C_2 to the lower and higher values of their practical industrial ranges, has naturally an effect on the reaction rates and effectiveness factors, but the percentage deviations between the predictions of the dusty-gas and the modified dusty-gas models, are similar to those given in Tables 1-3 [4].

CONCLUSION

The results of this note show that the effectiveness factors in the transition transport region for a second order reaction, predicted by the dusty-gas model are larger (up to about 30% for the systems examined) than those estimated by the modified dusty-gas model which accounts for the effects the pore-size and tortuosity distributions have on the mass fluxes in industrial heteroporous catalysts.

ACKNOWLEDGMENT

The authors express their appreciation to the Weldon Springs Fund of the University of Missouri for support of this work.

NOTATION

C_A ≡ concentration of component A, g-moles/cm^3

C_o ≡ constant dependent only upon structure of porous medium and giving relative D'Arcy flow permeability, cm^2

C_1 ≡ constant dependent only upon structure of porous medium and giving relative Knudsen flow permeability, cm

C_2 ≡ constant dependent only upon structure of porous medium and giving ratio of molecular diffusivity within the porous medium to the free gas diffusivity, dimensionless

k ≡ reaction constant

L ≡ length of catalyst pellet, cm

M_A ≡ molecular weight of A, g/g-mole

M_B ≡ molecular weight of B, g/g-mole

n ≡ order of the reaction

N_A ≡ molar flux of A, g-moles/cm^2-sec

N_B ≡ molar flux of B, g-moles/cm^2-sec

P ≡ total pressure, dyn/cm^2

r_A ≡ reaction rate of component A

R ≡ pore radius, Å

R_g ≡ gas constant, 8.317×10^7 erg/g-mole-°K

T ≡ absolute temperature, °K

V_p ≡ volume of catalyst pellet, cm^3

$V_1(R)$ ≡ volume percent of pores with radius, R, in porous medium 1 (Reference [2]), dimensionless

$V_2(R)$ ≡ volume percent of pores with radius, R, in porous medium 2 (Reference [2]), dimensionless

w ≡ z/LX_0, dimensionless length

X_0 ≡ z_0/L, dimensionless length at which $y_A = 0$

y_A ≡ mole fraction of component A, dimensionless

z ≡ distance in the direction of mass transfer, cm

z_0 ≡ distance in the pellet at which $y_A = 0$

GREEK SYMBOLS

α ≡ characteristic parameter of the function $\Delta(R)$ of Reference [2], $\mathring{A}^{-1}$

η ≡ effectiveness factor defined by equation (1), dimensionless

θ ≡ number of moles of B produced by one mole of A

ϕ_D ≡ diffusion-flow correction factor (Reference [2]), dimensionless

ϕ_{SA} ≡ slip-flow correction factor (Reference [2]), dimensionless

ϕ_{SB} ≡ slip-flow correction factor (Reference [2]), dimensionless

SUBSCRIPTS

DG ≡ dusty-gas model

MDG ≡ modified dusty-gas model

TABLE HEADINGS

Table 1. Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for $\theta=3$ and for a Second Order Reaction

Table 2. Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for $\theta=2$ and for a Second Order Reaction

Table 3. Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for $\theta=1/2$ and for a Second Order Reaction

TABLE 1

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for $\theta=3$ and for a Second Order Reaction

			$V_1(R)$		$V_2(R)$	
	$k\left(\frac{cm^3}{g\ moles\ sec}\right)$	η_{DG}	η_{MDG}	%DEV	η_{MDG}	%DEV
$\phi_D = \phi_{SA} = \phi_{SB} = 1.0$ (Dusty-Gas Model)	10.56×10^6	0.005580	—	—	—	—
$\alpha = 10^{-2}$	10.56×10^6	0.005580	0.003953	29.2	0.005313	4.8
$\alpha = 10^{-4}$	10.56×10^6	0.005580	0.005231	6.3	0.005484	1.7
$\alpha = 10^{-6}$	10.56×10^6	0.005580	0.005531	0.9	0.005554	0.5
$\alpha = 10^{-8}$	10.56×10^6	0.005580	0.005537	0.8	0.005556	0.4
$\alpha = 10^{-10}$	10.56×10^6	0.005580	0.005537	0.8	0.005556	0.4

$$\%DEV = \frac{\eta_{DG} - \eta_{MDG}}{\eta_{DG}} \times 100$$

TABLE 2

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for $\theta=2$ and for a Second Order Reaction

	$k\left(\frac{cm^3}{g\ moles\ sec}\right)$	η_{DG}	$V_1(R)$		$V_2(R)$	
			η_{MDG}	%DEV	η_{MDG}	%DEV
$\phi_D = \phi_{SA} = \phi_{SB} = 1.0$ (Dusty-Gas Model)	13.85×10^6	0.006469	—	—	—	—
$\alpha = 10^{-2}$	13.85×10^6	0.006469	0.004506	30.3	0.006132	5.2
$\alpha = 10^{-4}$	13.85×10^6	0.006469	0.006040	6.6	0.006346	1.9
$\alpha = 10^{-6}$	13.85×10^6	0.006469	0.006408	0.9	0.006435	0.5
$\alpha = 10^{-8}$	13.85×10^6	0.006469	0.006415	0.8	0.006438	0.5
$\alpha = 10^{-10}$	13.85×10^6	0.006469	0.006415	0.8	0.006438	0.5

$$\%\ DEV = \frac{\eta_{DG} - \eta_{MDG}}{\eta_{DG}} \times 100$$

TABLE 3

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for $\theta=1/2$ and for a Second Order Reaction

			$V_1(R)$		$V_2(R)$	
	$k(\frac{cm^3}{g\ moles\ sec})$	η_{DG}	η_{MDG}	%DEV	η_{MDG}	%DEV
$\phi_D = \phi_{SA} = \phi_{SB} = 1.0$ (Dusty-Gas Model)	17.31×10^6	0.009285	—	—	—	—
$\alpha = 10^{-2}$	17.31×10^6	0.009285	0.006484	30.2	0.008806	5.2
$\alpha = 10^{-4}$	17.31×10^6	0.009285	0.008674	6.6	0.009110	1.9
$\alpha = 10^{-6}$	17.31×10^6	0.009285	0.009199	0.9	0.009237	0.5
$\alpha = 10^{-8}$	17.31×10^6	0.009285	0.009209	0.8	0.009241	0.5
$\alpha = 10^{-10}$	17.31×10^6	0.009285	0.009209	0.8	0.009241	0.5

$$\%DEV = \frac{\eta_{DG} - \eta_{MDG}}{\eta_{DG}} \times 100$$

FIGURE CAPTIONS

Figure 1. Mass Flux and Coordinate Directions in One-Dimensional Catalyst Pellet.

Figure 2. Mass Flux of Component A versus Pellet Length for a Second Order Reaction with $\theta=2$ and Pore-Size Distribution $V_1(R)$.

Figure 3. Mass Flux of Component A versus Pellet Length for a Second Order Reaction with $\theta=2$ and Pore-Size Distribution $V_2(R)$.

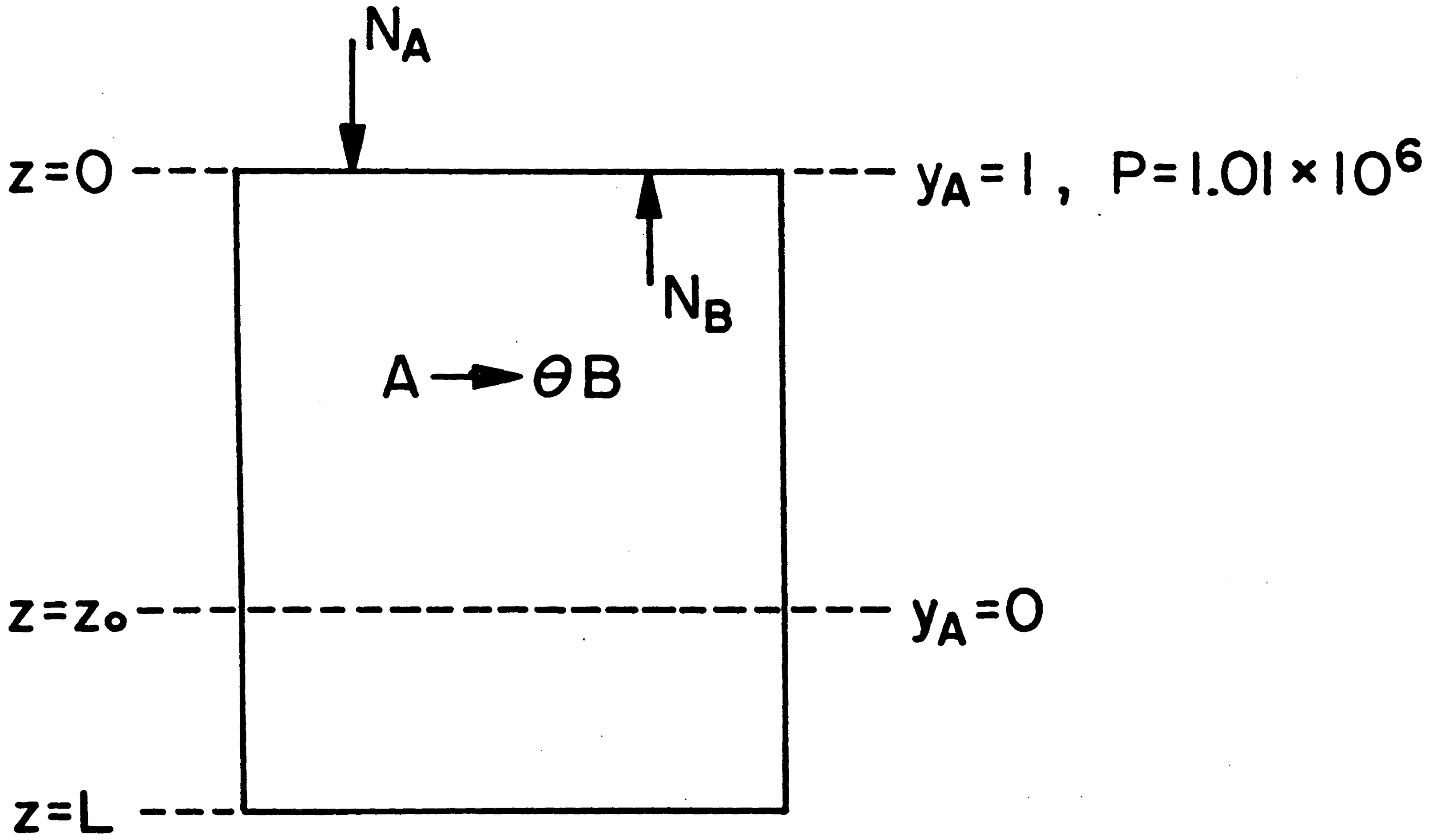

Figure 1.

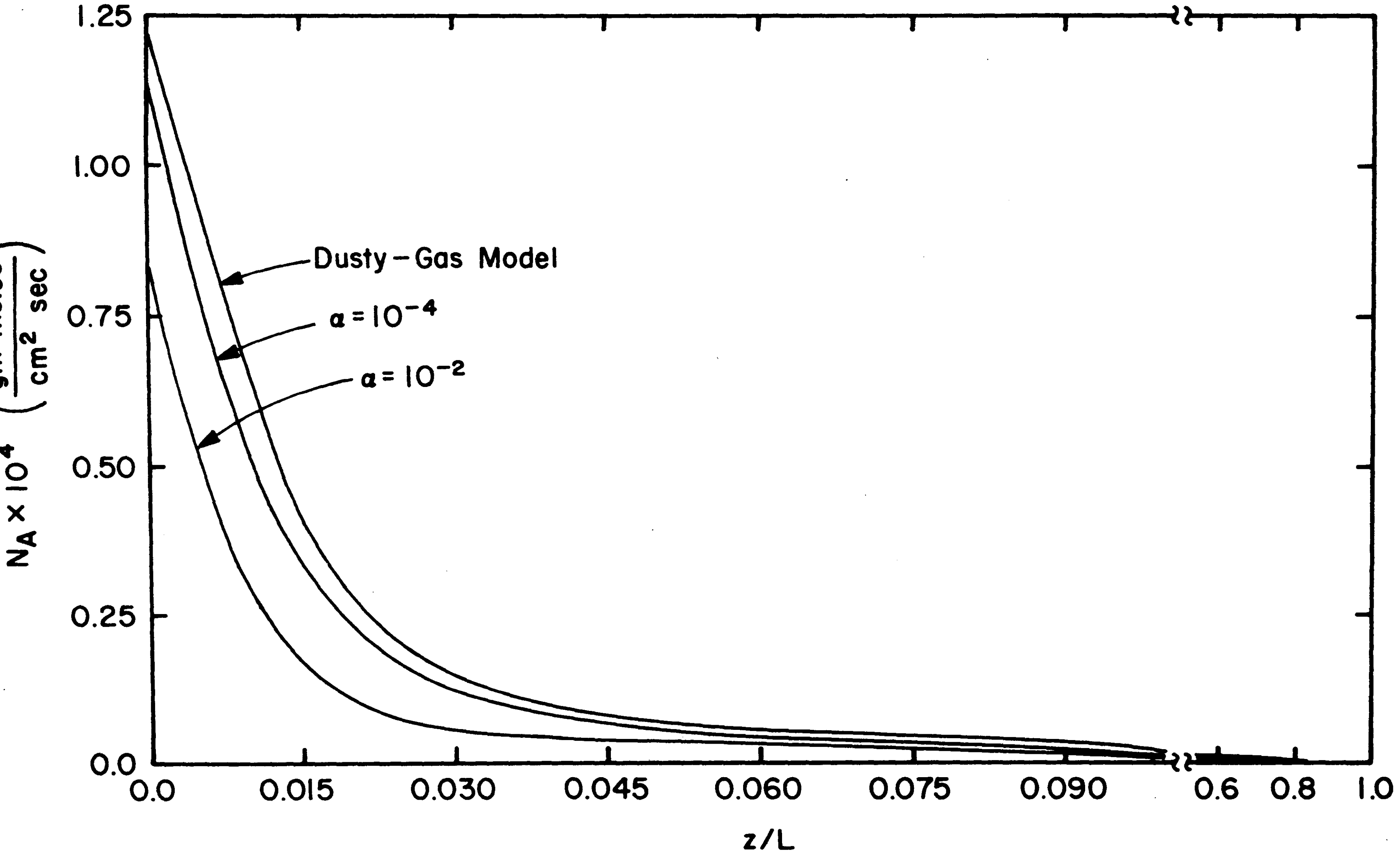
1.25
1.00
0.75
0.50
0.25
0.0
$N_A \times 10^4$ $\left(\frac{\text{gm moles}}{\text{cm}^2\ \text{sec}}\right)$
Dusty-Gas Model
$\alpha = 10^{-4}$
$\alpha = 10^{-2}$
0.0
0.015
0.030
0.045
0.060
0.075
0.090
0.6
0.8
1.0
z/L

Figure 2.

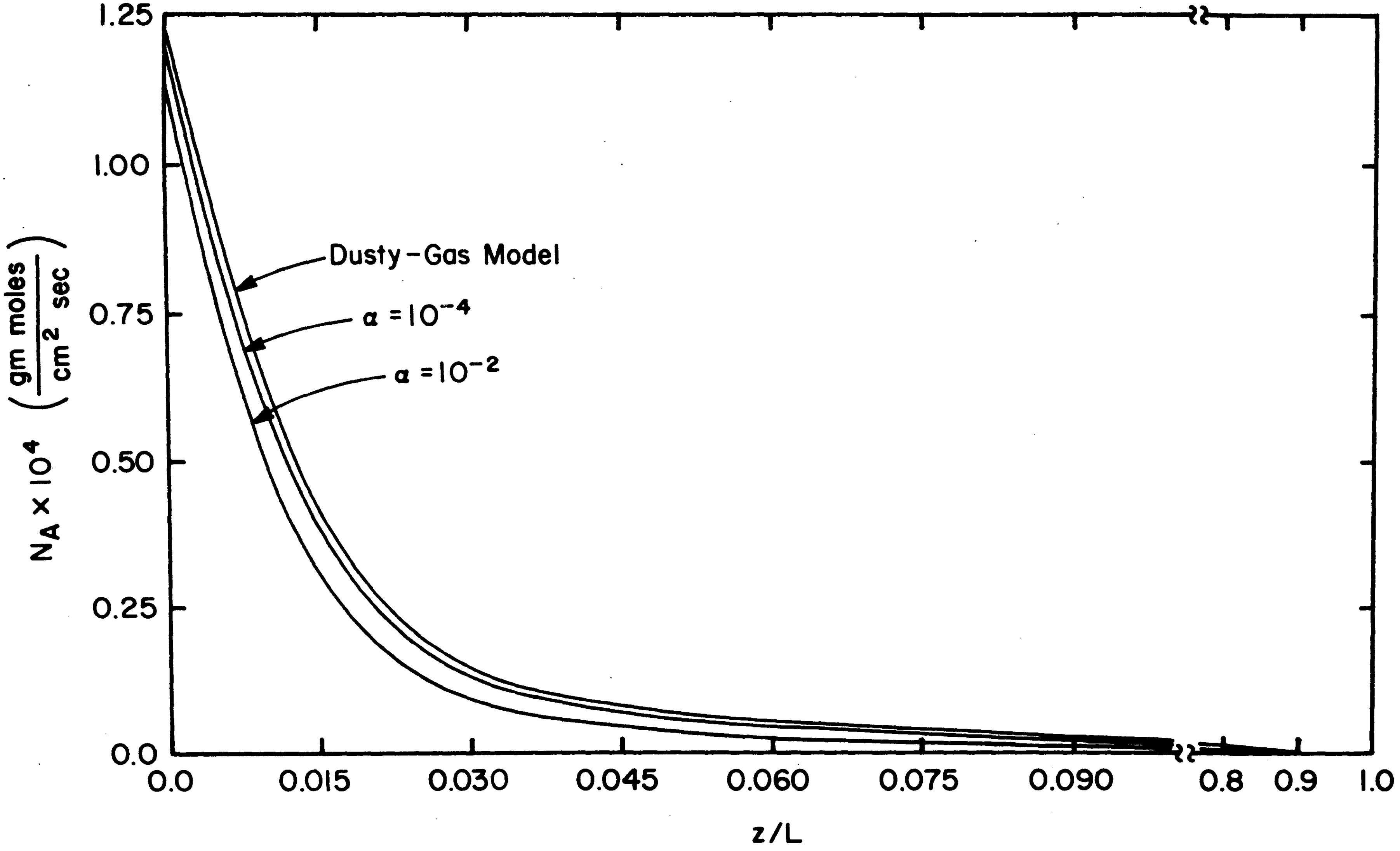
1.25
1.00
0.75
0.50
0.25
0.0
$N_A \times 10^4$ $\left(\frac{\text{gm moles}}{\text{cm}^2\ \text{sec}}\right)$
Dusty-Gas Model
$\alpha = 10^{-4}$
$\alpha = 10^{-2}$
0.0
0.015
0.030
0.045
0.060
0.075
0.090
0.8
0.9
1.0
z/L

Figure 3.

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VITA

Elmer Anthony Klavetter was born on March 9, 1959, in Minneapolis, Minnesota. He graduated from Park Hill High School in Kansas City, Missouri in May 1976. He entered the University of Missouri-Rolla in August, 1976, and received his Bachelor of Science degree in Chemical Engineering in 1980. Since June, 1980, he has been enrolled in the Graduate School of the University of Missouri-Rolla and has been the recipient of the Shell Foundation Fellowship. In 1981, he received a Master of Science degree in Chemical Engineering.

APPENDIX A

EXTENDED LITERATURE REVIEW

Although the estimation of effective diffusion coefficients and the characterization of mass transport in catalysts and other porous materials has received a great deal of attention in chemical engineering literature, the complications of multicomponent diffusion over a broad range of pressures and the insufficiently characterized porous structures make a rigorous solution not practicable (Jackson (1); Froment and Bischoff (2)). Even for the simplifying assumption of a single infinitely-long cylinder, diffusion in the transition regime between the limits of Knudsen diffusion and bulk diffusion has not been rigorously treated (Jackson (1); Gunn and King (3); Gavalas and Kim (4)).

In porous catalysts, membranes, and adsorbents, gas mixtures diffuse through a porous matrix composed of irregular channels of various sizes, ranging from pores of radii much smaller than the mean free path lengths of the gas molecules, to larger pores where the radii are much larger than the mean free path lengths. In order to model mass transfer in such porous structures, it is necessary to develop flux relations valid not only for the pores and operating conditions where the limiting cases of Knudsen diffusion and bulk diffusion occur, but also for the mass transport in the intermediate transition region. Although the theory of transport in porous media was advanced over a century ago by Maxwell (5), and the major fundamental physical phenomena of diffusion were studied by Graham (6-9) even earlier, it is only comparatively recently that detailed forms for the flux relations have been proposed and thought was given to their use in describing the behavior of mass transport in various porous media (Jackson (1); Froment and Bischoff (2); Gavalas and Kim (4); Aris (10)).

At the present time there exist no flux relations with a completely sound theoretical basis capable of describing transport behavior in porous materials over the whole range of pore geometries and operating conditions. The presently existing models tend to fall into two major classes: the first is where the porous structure itself is modelled, usually as a network of connected capillaries, while in the second class, the porous structure is represented as an assembly of stationary obstacles dispersed in the gas on a molecular scale. In the first approach, the porous media is visualized as a collection of cylindrical capillaries of various sizes, and flux relations for a single capillary are averaged with respect to the pore-size distribution to provide effective flux relations. These types of models have been developed by Johnson and Stewart (11), Feng and Stewart (12), Feng, Kostrov and Stewart (13), Gavalas and Kim (4), Satterfield and Cadle (14), Wheeler (16), and Gavalas (15). In this type of model, where the pore structure is viewed as an assembly of interconnected capillaries, the flux vectors are formed by adding contributions from the individual channels. So to accurately predict the behavior in porous catalysts by these models, equations must exist which will predict the fluxes in a single channel throughout the range of very small to very large diameters. Classical Knudsen theory gives equations for the fluxes in pores with very small diameters or at very low pressures, and continuum theory gives the fluxes for pores with large diameters or at high pressures. However, for the intermediate cases in the transition region, where the mean free path lengths are comparable to the pore diameters, there exists no adequate theory to predict the mass transport behavior (Jackson (1); Gunn and King (3)). Since many industrial catalysts have pore sizes in this intermediate range (Jackson (1)), the capillary flux model may be inadequate. Also, in the capillary models, many assumptions must be made and parameters introduced into the equations regarding the orientations, pattern of connections, and size distributions of the porous systems, which cannot be estimated by independent experiments.

The second type of model is more loosely related to the actual structure of the porous medium, but is more tractable theoretically and its predictions are in agreement with those of the capillary model approach. The main and most successful representative (Jackson (1)) is the dusty-gas model which was developed by Evans, Watson and Mason (17-19) and has gained considerable popularity because it does not make any assumptions about the pore geometry and involves only three physical parameters that characterize the porous media; Derjaguin and Bakanov (20) independently developed a similar model. The dusty-gas model has a firmer theoretical basis than other current models (Youngquist (21)) but can theoretically only predict the mass transport behavior of gases in homoporous, or unimodal, media. In the dusty-gas model, the porous medium is visualized as a collection of large dust particles which are considered to be giant molecules in the transport equations. Thus, the desired transport equations for a binary gas mixture diffusing through a porous body can be deduced by considering the entire system to be a ternary mixture composed of the binary gas components and the dust molecules. The dust molecules are constrained to be stationary in space and isotropic. Mason, Malinauskas and Evans (22) presented a generalized treatment of gas transport in porous media using the dusty-gas model by examining mass transport applicable to different operating conditions.

Evans, Watson and Truitt (23,24) made experimental investigations of the interdiffusion behavior of gases in a low permeability graphite and found that the dusty-gas model formed an excellent basis for correlating the results. Gunn and King (3) experimentally verified the ability of the dusty-gas model to predict mass transport behavior under combined gradients of composition and pressure in a fritted glass diaphragm. Abed and Rinker (25) made experimental studies of isobaric diffusion, permeability of pure gases, and simultaneous flow and binary diffusion in commercial catalytic pellets and attempted to correlate the data using the dusty-gas model. They found deviations in the experimental results and the predictions of the dusty-gas model due to the bimodal nature of the porous media used. Omata and Brown (26) also applied the dusty-gas model to isobaric diffusion in bimodal structures and found deviations between the computed and experimental fluxes. Liapis and Litchfield (27,28) have also applied the dusty-gas equations in modelling the freeze drying process. Jackson (1) favors the dusty-gas model as being more theoretically tractable than other flux models and it also provides the simplest effective method presently available for representing flow and diffusion throughout the intermediate region between the limits of Knudsen streaming and bulk diffusion with viscous flow, in homoporous media. It should be noted that heteroporous media possess pore-size and tortuosity distributions.

Wendt, Mason and Bresler (29) describe the effects of heteroporosity on flux equations for membranes; Kocirik and Zikanova (30) analyze the adsorption kinetics in materials with polydisperse pore structures; and Wakeham and Mason (31) discuss diffusion through lamina with a distributed array of pores. Kaza and Jackson (32) have discussed diffusion and reaction of multicomponent gas mixtures in porous catalysts under isothermal conditions using the dusty-gas model.

The dusty-gas model has been used as a basis for treating flux transport in porous membranes by Mason, Wendt and Bresler (33), Daneshpajooh, Mason, Bresler and Wendt (34), and Mehta, Morse, Mason and Daneshpajooh (35). Williams, Gonzalez and Laborde (36) have used the dusty-gas model to describe reaction in a catalytic pellet and examined the influence that the three physical geometric parameters have on the catalyst pellet effectiveness. Abed and Rinker (37) applied the dusty-gas model to reaction with mole changes in porous catalysts in the molecular, transition, and Knudsen regimes.

The deviations in the mass fluxes predicted by the dusty-gas model and the experimental mass fluxes where porous structures with bimodal pore-size distributions were used are not surprising since the dusty-gas model can theoretically predict mass transport behavior only in homoporous media (Jackson (1); Feng and Stewart (12); Scott and Dullien (38); Chen (39)). While there are capillary models that attempt to take into account the effects that a pore-size distribution has on the mass transport behavior in porous media, such as those developed by Feng and Stewart (12), those models still suffer the fundamental disadvantages previously described for the capillary approach.

Thus, in this work a modeling procedure is presented which modifies the dusty-gas model (Wendt, Mason and Bresler (29); Chen (39); Chen and Rinker (41)) in order to account for the effects the pore-size and tortuosity distributions have on the mass fluxes of heteroporous media, and also on the effectiveness factors of catalytic reactions which occur in permeable catalysts when Knudsen and molecular diffusion are present, as well as D'arcy flow. Comparisons for the mass fluxes and effectiveness factors for zero, first, and second order reactions as predicted by the dusty-gas and the modified dusty-gas models under varying operating conditions are also presented.

APPENDIX B

EXTENDED RESULTS AND DISCUSSION

A. INTRODUCTION

The modified dusty-gas model contains four physical parameters, C_0, C_1, C_2, and α, which are characteristic only of the porous medium. The parameter α is introduced into the dusty-gas model through the effectiveness function and thus through the diffusion and slip-flow correction factors. The publication in this work entitled "Comparison of Mass Fluxes Predicted by the Dusty-Gas and a Modified Dusty-Gas Model" (hereafter referred to as Paper I) presents results showing how the parameter α, the pore-size distribution, and the pressure affect the mass fluxes predicted by the modified dusty-gas model relative to those of the dusty-gas model for binary isobaric diffusion and simultaneous diffusion and flow. The publications entitled "Chemical Reactions with Mole Changes in Heteroporous Catalysts - Part I" and "Chemical Reactions with Mole Changes in Heteroporous Catalysts - Part II" (hereafter referred to as Paper II and Paper III, respectively) present results showing how α, the pore-size distribution, reaction stoichiometry, and reaction order affect the modified dusty-gas model's predictions relative to those predicted by the dusty-gas model when an irreversible gaseous reaction in a heteroporous medium is considered.

In Paper I, various values of the parameter α are tested with two different pore-size distributions. The diffusion correction factors as functions of pressure are presented for three values of α for both pore-size distributions in Figure 3 of Paper I.

The diffusion correction factors as functions of pressure for the remaining two tested values of $\alpha = 1 \times 10^{-6}$ and $\alpha = 1 \times 10^{-10}$ for both pore-size distributions are shown here in Figure B-1. For both pore-size distributions, as α decreases, the correction factors approach unity at all pressures. The slip-flow correction factors for $\alpha = 1 \times 10^{-2}$ and $\alpha = 1 \times 10^{-8}$ are presented in Figures 4 and 5, respectively, of Paper I. The slip-flow correction factors as functions of pressure are presented in Figure B-2 for $\alpha = 2 \times 10^{-4}$. At any particular pressure, there is no distinguishable difference in the values of the slip-flow correction factors for α less than 10^{-6}.

The results presented in the body of this work emphasize the effects that α, the pore-size distribution, and the pressure have on the mass fluxes. In this appendix, more extensive results are presented showing the effects that variations in the other physical parameters have on the mass fluxes for both the dusty-gas and the modified dusty-gas models for the following isothermal cases:

(1) Binary isobaric diffusion
(2) Simultaneous diffusion and flow
(3) Irreversible chemical reactions with mole changes

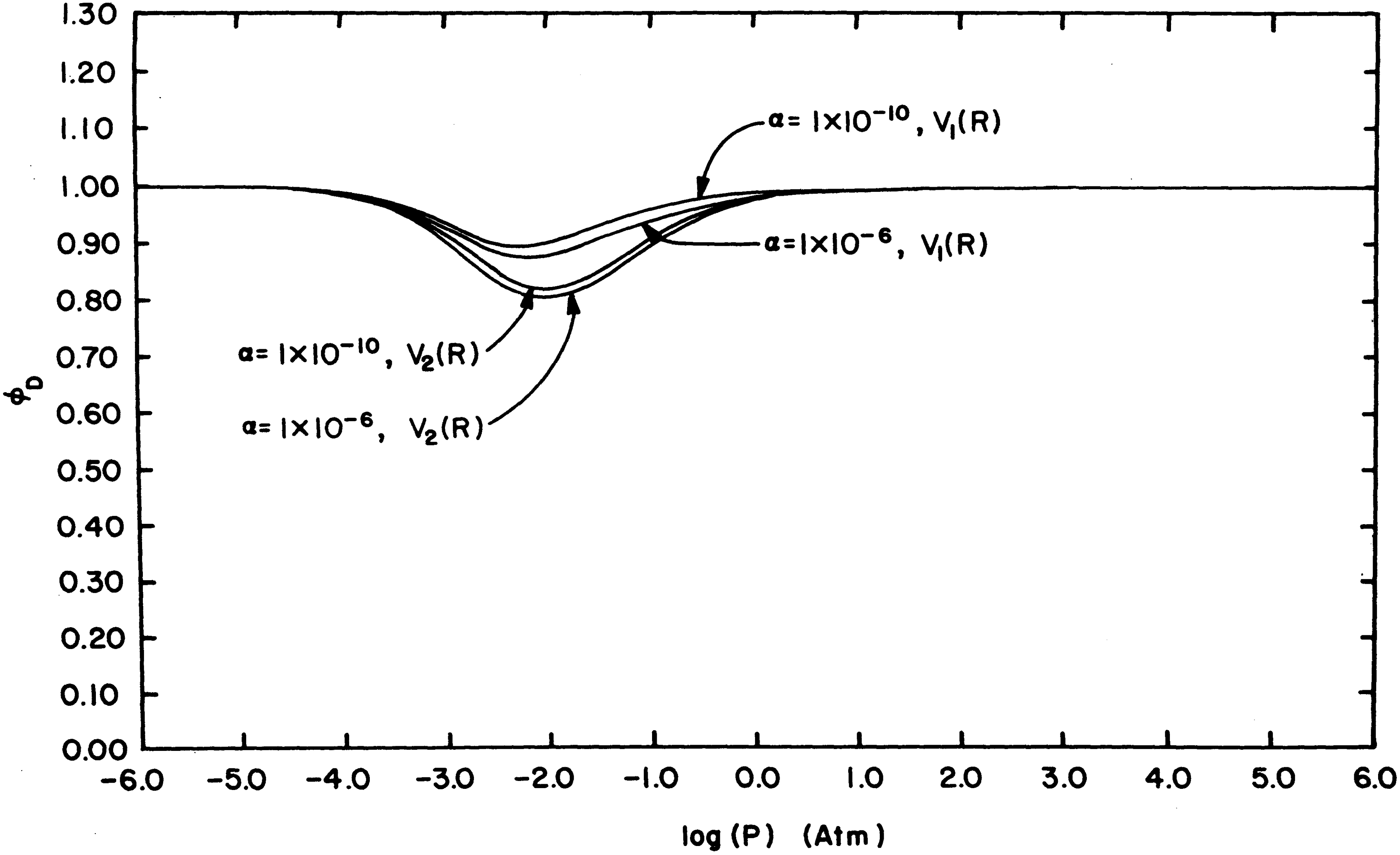

Figure B-1. The Effect of Pressure on the Diffusion-Flow Correction Factor

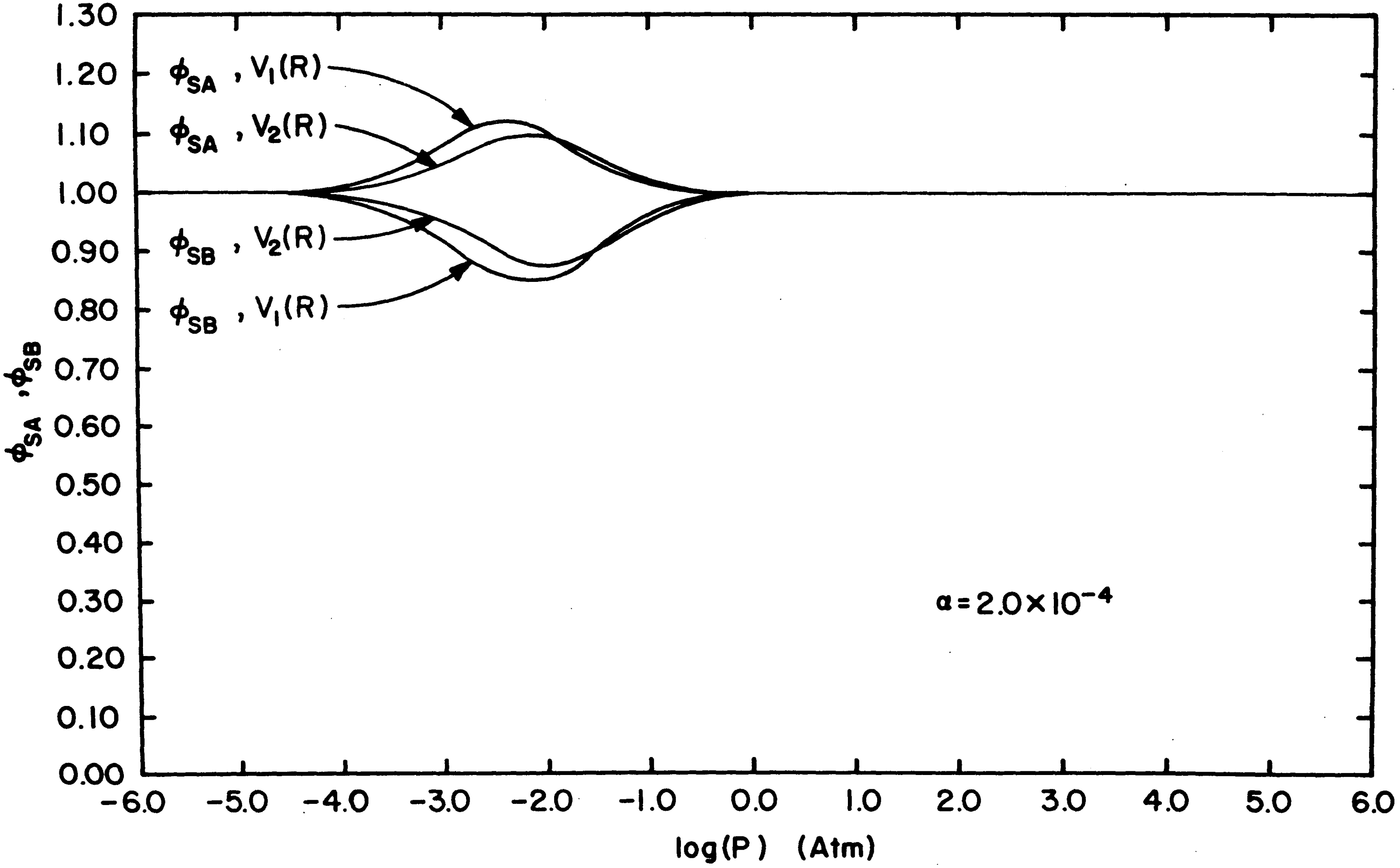

Figure B-2. The Effect of Pressure on the Slip-Flow Correction Factors

B. BINARY ISOBARIC DIFFUSION

The results given in Paper I for the case of binary isobaric diffusion show the deviation in the mass fluxes of component A predicted by the modified dusty-gas model relative to the mass fluxes predicted by the dusty-gas model for pressures ranging from 1-20 atm, for values of the parameter α ranging from 10^{-2} - 10^{-10} and for two pore-size distributions. These results were obtained with the two physical parameters C_1 and C_2 constant at $C_1 = 2000 \times 10^{-8}$ and $C_2 = 0.5$. Included in this appendix are results for other combinations of the physical parameters.

The percentage deviation of the mass flux of component A (or component B) for the two models is independent of the values of C_1 and C_2, since

$$N_{A,MDG} = \phi_D N_{A,DG} \qquad (1)$$

Therefore, the deviation in the mass fluxes is proportional only to the deviation of the diffusion correction factor from unity, and so the modified dusty-gas model changes the magnitude of the flux as predicted by the dusty-gas model but does not alter how the flux changes with respect to the geometric parameters C_1 and C_2.

As C_2 varies from 0.1 - 0.8, the relative change in N_A (or N_B) is the same for both the modified dusty-gas model and the dusty-gas model, since

$$\left.\frac{(N_A)_{C_2=0.8} - (N_A)_{C_2=0.1}}{(N_A)_{C_2=0.8}}\right|_{MDG} = \left.\frac{(N_A)_{C_2=0.8} - (N_A)_{C_2=0.1}}{(N_A)_{C_2=0.8}}\right|_{DG} \quad (2)$$

The same result is true for the relative change in N_A as C_1 varies in its range of values of 50 x 10^{-8} to 2000 x 10^{-8} cm.

Although the relative change in the mass flux is the same for both models over the range of values for C_2, the absolute magnitude of the change in $N_{A,MDG}$ can differ greatly as compared to the change in the absolute magnitude of $N_{A,DG}$ over the same range of values. This can be seen from the results shown in Table B-1, where the mass fluxes of component A are presented for the extreme values of C_2=0.1 and C_2=0.8. Since the percentage deviation is the same at both extremes of C_2, all other parameters being the same, the relative change in N_A must be the same for both the modified dusty-gas and the dusty-gas models for any value of C_2. However, the absolute magnitude of the change in N_A predicted by the modified dusty-gas model over the range $0.1 \leq C_2 \leq 0.8$ differs by over 66% (for $\alpha = 10^{-2}$; P = 1 atm) of the change in the value of N_A predicted by the dusty-gas model for the cases tested.

Similar results were obtained when C_1 was varied from 50 x 10^{-8} to 2000 x 10^{-8} as shown by the results presented in Table B-2. Therefore, while the manner of the change in the flux is the same for both models as C_1 or C_2 is varied, the actual changes in the absolute magnitude of the mass fluxes could be significantly different.

TABLE B-1

Binary Isobaric Diffusion; $V_1(R)$ and $C_1 = 2000 \times 10^{-8}$

		$C_2 = 0.1$		$C_2 = 0.8$	
α	P(Atm)	$N_{A_{MDG}} \times 10^5$	% Dev N_A	$N_{A_{MDG}} \times 10^5$	% Dev N_A
1×10^{-2}	1	0.089	66.46	0.461	66.46
	6	0.168	40.69	1.221	40.69
	10	0.191	32.63	1.446	32.63
	14	0.206	27.56	1.583	27.56
	20	0.221	22.56	1.717	22.56
2×10^{-4}	1	0.195	26.10	1.015	26.10
	6	0.252	10.78	1.837	10.78
	10	0.262	7.84	1.978	7.84
	14	0.267	6.25	2.049	6.25
	20	0.272	4.85	2.109	4.85
1×10^{-6}	1	0.258	2.29	1.342	2.29
	6	0.280	0.82	2.042	0.82
	10	0.283	0.58	2.133	0.58
	14	0.284	0.46	2.176	0.46
	20	0.284	0.35	2.209	0.35
1×10^{-8}	1	0.259	1.86	1.348	1.86
	6	0.281	0.66	2.045	0.66
	10	0.283	0.47	2.136	0.47
	14	0.284	0.37	2.178	0.37
	20	0.285	0.29	2.210	0.29
1×10^{-10}	1	0.259	1.86	1.348	1.86
	6	0.281	0.66	2.045	0.66
	10	0.283	0.47	2.136	0.47
	14	0.284	0.37	2.178	0.37
	20	0.285	0.28	2.210	0.28

$$\% \text{ Dev } N_A = \frac{N_{A_{DG}} - N_{A_{MDG}}}{N_{A_{DG}}} \times 100$$

TABLE B-2

Binary Isobaric Diffusion; $V_1(R)$ and $C_2 = 0.5$

		$C_1 = 50 \times 10^{-8}$		$C_1 = 2000 \times 10^{-8}$	
α	P(Atm)	$N_{A_{MDG}} \times 10^5$	% Dev N_A	$N_{A_{MDG}} \times 10^5$	% Dev N_A
1×10^{-2}	1	0.028	66.46	0.338	66.46
	6	0.228	40.69	0.793	40.69
	10	0.364	32.63	0.926	32.63
	14	0.475	27.56	1.007	27.56
	20	0.605	22.56	1.086	22.56
2×10^{-4}	1	0.062	26.10	0.745	26.10
	6	0.343	10.78	1.193	10.78
	10	0.498	7.84	1.266	7.84
	14	0.615	6.25	1.304	6.25
	20	0.743	4.85	1.335	4.85
1×10^{-6}	1	0.082	2.29	0.985	2.29
	6	0.381	0.82	1.327	0.82
	10	0.538	0.58	1.366	0.58
	14	0.653	0.46	1.384	0.46
	20	0.779	0.35	1.398	0.35
1×10^{-8}	1	0.082	1.86	0.989	1.86
	6	0.382	0.66	1.329	0.66
	10	0.538	0.47	1.368	0.47
	14	0.654	0.37	1.385	0.37
	20	0.779	0.29	1.399	0.29
1×10^{-10}	1	0.082	1.86	0.989	1.86
	6	0.382	0.66	1.329	0.66
	10	0.538	0.47	1.368	0.47
	14	0.654	0.37	1.385	0.37
	20	0.779	0.28	1.399	0.28

$$\% \text{ Dev } N_A = \frac{N_{A_{DG}} - N_{A_{MDG}}}{N_{A_{DG}}} \times 100$$

Additional results of the effects that different combinations of values of the parameters C_1, C_2, P and α have on the mass fluxes and concentration profiles predicted by both the modified dusty-gas and the dusty-gas models for isothermal binary isobaric diffusion may be obtained through the Chemical Engineering Department at the University of Missouri-Rolla.

C. SIMULTANEOUS DIFFUSION AND FLOW

In the case of simultaneous diffusion and flow, there is a contribution to the mass flux due to both a concentration and pressure gradient. The addition of the flow phenomena due to a pressure gradient introduces the additional parameters C_0, the pressure drop ΔP, and the slip-flow correction factors into the modified dusty-gas equations in addition to those parameters already present in the equations for binary isobaric diffusion. In addition to changing the pore-size distribution, the variation of the parameters C_0, C_1, C_2, α, ΔP and P_0 affects the mass fluxes predicted by the modified dusty-gas and the dusty-gas models. Included here are results of the mass fluxes predicted by both models for various combinations of the above mentioned parameters as they are varied over their range of tested industrial values.

Table 3 in Paper I shows predicted mass fluxes for both pore-size distributions for a range of pressures and values of the parameter α. As the pressure increases to the high pressure region, the deviation in the mass fluxes predicted by the modified dusty-gas model with respect to those predicted by the dusty-gas model decreases. For the pore-size distributions tested, the deviation decreases since a greater fraction of molecules are forced into the limiting region of molecular diffusion as the pressure increases and thus the modified dusty-gas model predicts results closer to those of the dusty-gas model. This would also be the case if the pressure was low enough that the molecules would be in the limiting Knudsen regime. As the parameter α decreases, the correction factors approach unity and the deviation in the mass fluxes predicted by the two models decreases for the whole pressure range considered. For the two pore-size distributions considered in this work, the largest deviation occurs at the highest value of α.

The parameter C_0 is a factor characteristic of the scale and geometry of the pore structure and is known as the permeability of the medium. In a porous structure, C_0 is on the order of magnitude of the square of the pore radii. The value of C_0 gives an indication of the degree of indirect transfer of momentum to the wall via a sequence of molecule-molecule collisions, terminating in a molecule-wall collision. Table B-3 shows mass fluxes predicted by the modified dusty-gas and dusty-gas models for two values of C_0 near the limits of their industrial range of values. As C_0 varies from 25×10^{-12} to 500×10^{-12}, the change in magnitude of the mass fluxes is approximately the same for both models. As the value of C_0 increases, the magnitude of the mass flux of component A decreases and that of component B increases. Since the molecular weight of component B is much less than that of component A, the mean free path length of B is greater and increasing C_0 increases the number of collisions involving component B and thus the mass flux of component B increases. Since the mean free path length of component A is already much shorter than that of component B, increasing C_0 does not significantly increase the collisions of A and, in fact, the axial mass flux of A decreases since the collisions of B become dominant.

TABLE B-3

Predicted Mass Fluxes for Components A and B by the Modified Dusty-Gas and the Dusty-Gas Models; Simultaneous Diffusion and Flow with C_o Varying

		$V_1(R)$				$V_2(R)$			
α	C_o	$N_A \times 10^5$	$N_B \times 10^5$	%DEV N_A	%DEV N_B	$N_A \times 10^5$	$N_B \times 10^5$	%DEV N_A	%DEV N_B
Dusty-Gas Model ($\Phi_D=\Phi_{SA}=\Phi_{SB}=1$)	25×10^{-12}	0.900	2.726	--	--	0.900	2.726	--	--
	500×10^{-12}	0.604	3.287	--	--	0.604	3.287	--	--
2×10^{-4}	25×10^{-12}	0.624	1.994	30.7	26.9	0.792	2.438	12.1	10.6
	500×10^{-12}	0.346	2.574	42.7	21.7	0.502	3.005	17.0	8.6
1×10^{-8}	25×10^{-12}	0.872	2.650	3.2	2.8	0.877	2.664	2.6	2.3
	500×10^{-12}	0.577	3.212	4.5	2.3	0.587	3.226	3.7	1.9

$$\%\text{DEV } N_i = \frac{N_{i_{DG}} - N_{i_{MDG}}}{N_{i_{DG}}} \times 100$$

$C_1 = 1000 \times 10^{-8}$, $C_2 = 0.8$, $\Delta P = P_o - P_L = 0.053$ atm, $P_o = 1$ atm

The percentage deviation of the predictions of the modified dusty-gas model with respect to those of the dusty-gas model are in the same magnitude range as C_0 varies. Again, the deviation is less at lower values of α and less for $V_2(R)$. The deviation of component B is less than that of component A since the absolute magnitude of N_B is greater than that of N_A.

The geometric factor C_1 is characteristic of the Knudsen permeability and the mass flux of both components increases as C_1 is increased over the range $50 \times 10^{-8} \leq C_1 \leq 2000 \times 10^{-8}$. Predicted mass fluxes for $C_1 = 50 \times 10^{-8}$ and $C_1 = 2000 \times 10^{-8}$ for the modified dusty-gas and the dusty-gas models are shown in Table B-4. Increasing C_1 characterizes a porous structure with a greater capability for diffusion in the pores and so the mass fluxes for both components increase. The results in Table B-4 are shown for the dusty-gas model and for the modified dusty-gas model for both pore-size distributions at two values of the parameter α.

Similar results were obtained as C_2 was varied in the range $0.1 \leq C_2 \leq 0.8$, as shown in Table B-5. The magnitude of the fluxes of both components increases as C_2 is increased from 0.1 to 0.8 and the deviation of the mass fluxes predicted by the two models as C_2 is varied are similar.

With both diffusion and flow, there is a pressure drop along the pellet length. Table B-6 shows the effects of changing the pressure drop from 0.053 atm to 0.132 atm (40 mm Hg to 100 mm Hg) for the dusty-gas and modified dusty-gas models at two values of α and for both pore-size distributions. Since component B diffuses in the

TABLE B-4

Predicted Mass Fluxes for Components A and B by the Modified Dusty-Gas and the Dusty-Gas Models; Simultaneous Diffusion and Flow with C_1 Varying

		$V_1(R)$				$V_2(R)$			
α	C_1	$N_A \times 10^5$	$N_B \times 10^5$	%DEV N_A	%DEV N_B	$N_A \times 10^5$	$N_B \times 10^5$	%DEV N_A	%DEV N_B
Dusty-Gas Model ($\phi_D=\phi_{SA}=\phi_{SB}=1$)	50×10^{-8}	0.061	0.249	--	--	0.061	0.249	--	--
	2000×10^{-8}	0.873	2.917	--	--	0.873	2.917	--	--
2×10^{-4}	50×10^{-8}	0.039	0.189	36.9	24.4	0.052	0.225	14.6	9.6
	2000×10^{-8}	0.589	2.166	32.5	25.8	0.761	2.622	12.8	10.1
1×10^{-8}	50×10^{-8}	0.059	0.243	3.9	2.5	0.059	0.244	3.2	2.1
	2000×10^{-8}	0.843	2.839	3.4	2.7	0.849	2.853	2.8	2.2

$$\%\text{DEV } N_i = \frac{N_{i_{DG}} - N_{i_{MDG}}}{N_{i_{DG}}} \times 100$$

$C_o = 25 \times 10^{-12}$, $C_2 = 0.5$, $\Delta P = P_o - P_L = 0.053$ atm, $P_o = 1$ atm

TABLE B-5

Predicted Mass Fluxes for Components A and B by the Modified Dusty-Gas and the Dusty-Gas Models; Simultaneous Diffusion and Flow with C_2 Varying

		$V_1(R)$				$V_2(R)$			
α	C_2	$N_A \times 10^5$	$N_B \times 10^5$	%DEV N_A	%DEV N_B	$N_A \times 10^5$	$N_B \times 10^5$	%DEV N_A	%DEV N_B
Dusty-Gas Model $(\phi_D=\phi_{SA}=\phi_{SB}=1)$	0.1	0.173	0.798	--	--	0.173	0.798	--	--
	0.8	0.900	2.726	--	--	0.900	2.726	--	--
2×10^{-4}	0.1	0.106	0.618	38.9	22.5	0.147	0.727	15.4	8.9
	0.8	0.624	1.994	30.7	26.9	0.792	2.438	12.1	10.6
1×10^{-8}	0.1	0.166	0.779	4.1	2.4	0.168	0.783	3.3	1.9
	0.8	0.872	2.650	3.2	2.8	0.877	2.664	2.6	2.3

$$\%\text{DEV } N_i = \frac{N_{i_{DG}} - N_{i_{MDG}}}{N_{i_{DG}}} \times 100$$

$C_o = 25 \times 10^{-12}$, $C_1 = 1000 \times 10^{-8}$, $\Delta P = P_o - P_L = 0.053$ atm, $P_o = 1$ atm

TABLE B-6

Predicted Mass Fluxes for Components A and B by the Modified Dusty-Gas and the Dusty-Gas Models; Simultaneous Diffusion and Flow with ΔP Varying

		$V_1(R)$				$V_2(R)$			
α	ΔP	$N_A \times 10^5$	$N_B \times 10^5$	%DEV N_A	%DEV N_B	$N_A \times 10^5$	$N_B \times 10^5$	%DEV N_A	%DEV N_B
Dusty-Gas Model ($\phi_D=\phi_{SA}=\phi_{SB}=1$)	0.053	0.700	2.196	--	--	0.700	2.196	--	--
	0.132	0.587	2.398	--	--	0.587	2.398	--	--
2×10^{-4}	0.053	0.481	1.614	31.3	26.5	0.614	1.967	12.3	10.4
	0.132	0.372	1.825	36.7	23.9	0.501	2.169	14.7	9.6
1×10^{-8}	0.053	0.677	2.135	3.3	2.8	0.682	2.146	2.7	2.3
	0.132	0.564	2.338	3.9	2.5	0.568	2.348	3.2	2.1

$$\%\text{DEV } N_i = \frac{N_{i_{DG}} - N_{i_{MDG}}}{N_{i_{DG}}} \times 100$$

$C_o = 25 \times 10^{-12}$, $C_1 = 1000 \times 10^{-8}$, $C_2 = 0.5$, $P_o = 1$ atm same direction as the pressure drop, the mass flux of B increases as the pressure drop increases and the mass flux of A decreases. As before, the percentage deviation between the two models decreases as α decreases and is less for $V_2(R)$.

Since the values of the mole fraction and pressure are set at both ends of the pellet by the boundary conditions, varying C_o, C_1, C_2, P or α has relatively little effect on the shape of the concentration or pressure profiles. Additional results of the effects that different combinations of the values of the parameters C_o, C_1, C_2, P, ΔP and α have on the mass fluxes, concentration profiles, and pressure profiles predicted by both the modified dusty-gas and dusty-gas models for both pore-size distributions, for the case of isothermal simultaneous diffusion and flow, may be obtained through the Chemical Engineering Department at the University of Missouri-Rolla.

D. IRREVERSIBLE CHEMICAL REACTIONS WITH MOLE CHANGES

The dusty-gas and modified dusty-gas models are used to predict the mass fluxes for zero, first and second-order isothermal, irreversible reactions with mole changes in heteroporous catalysts, and to estimate their effectiveness factors in the transition region where a majority of the pores exhibit transport behavior combining the simultaneous effects of ordinary molecular diffusion and Knudsen diffusion. The irreversible reactions have the form:

$$A \rightarrow \theta B \tag{3}$$

Paper II shows predicted effectiveness factors by the dusty-gas and modified dusty-gas models for $V_1(R)$ and $V_2(R)$ for zero and first-order reactions with $\theta = \frac{1}{2}$, 2, and 3, and for various values of the parameter α. Paper III shows similar results for a second-order reaction. Median industrial values of the physical parameters C_0, C_1, and C_2 were used. An external pressure of one atmosphere was used in all calculations, as well as a pellet length of one centimeter.

Papers II and III show that, as in the cases of binary isobaric diffusion and simultaneous diffusion and flow, when the value of α decreases, the percentage deviation of the effectiveness factors predicted by both models also decreases. As in the other cases, the deviation at any value of α is less for $V_2(R)$ than for $V_1(R)$. Although only one pressure value was tested, it would be expected that the deviation between the predictions of the two models would be small at either very high or very low pressures.

The value of θ has only a minor effect on the percentage deviation of the effectiveness factors predicted, although its value does affect the concentration and pressure profiles. The value of θ is determined by the ratio of molecular weights of the two components in the reacting system. To achieve the tested values of $\theta = \frac{1}{2}$, 2, and 3, molecular weights of 16, 32, and 48 were used ($\theta = \frac{1}{2} = \frac{16}{32}$; $\theta = 2 = \frac{32}{16}$; $\theta = 3 = \frac{48}{16}$). The physical properties used, corresponding to these molecular weights, are shown in Table B-7. The value of θ has only a small effect on the shape of the concentration profile since the boundary conditions determine the values of the mole fractions at the ends of the pellet. For $\theta > 1$, the internal pressure in the porous structure increases since the number of moles of gas increase due to the reaction. For $\theta < 1$, the internal pressure decreases as the reaction progresses. For any of the values of θ tested, however, there is less than a one percent change in the pressure and thus varying θ does not cause a significant difference in the pressure values along the pellet length, assuming all other parameters are kept constant.

The physical properties for the three compounds shown in Table B-7 were used to calculate the heteroporosity diffusion and slip-flow correction factors for $\theta = \frac{1}{2}$, 2, and 3 for both pore-size distributions. The correction factors for $\theta = 3$ for the various tested values of α are shown in Table B-8 for both $V_1(R)$ and $V_2(R)$. The correction factors shown are for $P = 1$ atm. Since there is only a small pressure gradient, there is only a minor variation in the

TABLE B-7

Physical Properties of the Reacting Components

Molecular Weight	T_c	P_c	μ(g/cm sec)
16	190	60	140×10^{-6}
32	310	50	120×10^{-6}
48	380	45	110×10^{-6}

TABLE B-8

Heteroporosity Correction Factors For
$\theta = 3$ and $P = 1$ Atm
($M.W._A = 48$, $M.W._B = 16$)

	$V_1(R)$			$V_2(R)$		
α	ϕ_D	ϕ_{SA}	ϕ_{SB}	ϕ_D	ϕ_{SA}	ϕ_{SB}
1×10^{-2}	0.5037	1.00321	0.99453	0.9070	1.00023	0.99960
1×10^{-4}	0.8797	1.00013	0.99978	0.9659	1.00005	0.99992
1×10^{-6}	0.9825	1.00001	0.99999	0.9906	1.00000	0.99999
1×10^{-8}	0.9846	1.00000	0.99999	0.9914	1.00000	0.99999
1×10^{-10}	0.9846	1.00000	0.99999	0.9914	1.00000	0.99999

values of the correction factors as the reaction progresses through the pellet. The correction factors for $\theta = 2$ are shown in Table B-9, also at one atmosphere. The correction factors for $\theta = \frac{1}{2}$ are the same as for $\theta = 2$ if the subscripts of A and B are switched for the slip-flow correction factors.

The variation of the parameters C_0, C_1, and C_2 in their range of values, shown in Table 1 of Paper I, has an effect on the mass fluxes of both components and on the values of the effectiveness factors, but has only a minor effect on the percentage deviation of these quantities as predicted by the dusty-gas and modified dusty-gas models. These results are shown in Table B-10 when C_0 is varied, in Table B-11 when C_1 is varied, and in Table B-12 when C_2 is varied. Two values of each of the three geometric parameters at the extremes of their range of values were tested for the dusty-gas model ($\phi_D=\phi_{SA}=\phi_{SB}=1$) and for $\alpha = 10^{-2}$ for $V_1(R)$ and for a zero-order reaction. Although the mass fluxes and effectiveness factors change as the parameters change, the percentage deviation in the effectiveness factors with $\alpha = 10^{-2}$ remains at approximately 30%. As noted previously, changing the order of the reaction has a negligible effect on the percentage deviation between the predictions of the dusty-gas and of the modified dusty-gas models.

Therefore, although changing C_0, C_1, C_2, θ, or the order of the reaction does produce changes in the magnitudes of the mass fluxes and effectiveness factors predicted by the dusty-gas and the

TABLE B-9

Heteroporosity Correction Factors for
$\theta = 2$ and P = 1 Atm
($M.W._A = 32$, $M.W._B = 16$)

α	$V_1(R)$ ϕ_D	$V_1(R)$ ϕ_{SA}	$V_1(R)$ ϕ_{SB}	$V_2(R)$ ϕ_D	$V_2(R)$ ϕ_{SA}	$V_2(R)$ ϕ_{SB}
1×10^{-2}	0.4862	1.00257	0.99640	0.8989	1.00019	0.99973
1×10^{-4}	0.8720	1.00010	0.99985	0.9624	1.00004	0.99994
1×10^{-6}	0.9813	1.00000	0.99999	0.9896	1.00000	0.99999
1×10^{-8}	0.9836	1.00000	0.99999	0.9904	1.00000	1.00000
1×10^{-10}	0.9836	1.00000	0.99999	0.9904	1.00000	1.00000

TABLE B-10

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for $\theta=2$, $V_1(R)$, and a Zero Order Reaction; C_o Varies

	$C_o = 25 \times 10^{-12}$		$C_o = 1000 \times 10^{-12}$	
	Dusty-Gas Model	$\alpha = 10^{-2}$	Dusty-Gas Model	$\alpha = 10^{-2}$
$k(\frac{\text{g moles}}{\text{cm}^3\ \text{sec}})$	4.741×10^{-6}	4.741×10^{-6}	4.741×10^{-6}	4.741×10^{-6}
$N_A\Big\vert_{z=0}\ (\frac{\text{g moles}}{\text{cm}^2\ \text{sec}})$	4.23×10^{-6}	2.94×10^{-6}	4.15×10^{-6}	2.89×10^{-6}
η	0.9010	0.6307	0.8997	0.6274
% DEV	--	30.0	--	30.3

$$\% \text{ DEV} = \frac{\eta_{DG} - \eta_{MDG}}{\eta_{DG}} \times 100$$

$C_1 = 1000 \times 10^{-8}$, $C_2 = 0.5$, $P = 1$ atm

TABLE B-11

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for $\theta=2$, $V_1(R)$, and for a Zero Order Reaction; C_1 Varies

	$C_1 = 50 \times 10^{-8}$		$C_1 = 2000 \times 10^{-8}$	
	Dusty-Gas Model	$\alpha = 10^{-2}$	Dusty-Gas Model	$\alpha = 10^{-2}$
$k(\frac{\text{g moles}}{\text{cm}^3 \text{ sec}})$	4.741×10^{-6}	4.741×10^{-6}	4.741×10^{-6}	4.741×10^{-6}
$N_A\big\vert_{z=0}$ $(\frac{\text{g moles}}{\text{cm}^2 \text{ sec}})$	1.87×10^{-6}	1.30×10^{-6}	4.40×10^{-6}	3.06×10^{-6}
η	0.4051	0.2821	0.9502	0.6632
% DEV	--	30.4	--	30.2

$$\% \text{ DEV} = \frac{\eta_{DG} - \eta_{MDG}}{\eta_{DG}} \times 100$$

$C_o = 500 \times 10^{-12}$, $C_2 = 0.5$, $P = 1$ atm

TABLE B-12

Predicted Effectiveness Factors by the Dusty-Gas and the Modified Dusty-Gas Models for $\theta=2$, $V_1(R)$, and for a Zero Order Reaction; C_2 Varies

	$C_2 = 0.1$		$C_2 = 0.8$	
	Dusty-Gas Model	$\alpha = 10^{-2}$	Dusty-Gas Model*	$\alpha = 10^{-2}$
$k(\frac{\text{g moles}}{\text{cm}^3\ \text{sec}})$	4.741×10^{-6}	4.741×10^{-6}	4.741×10^{-6}	4.741×10^{-6}
$N_A\Big\|_{z=0}\ (\frac{\text{g moles}}{\text{cm}^2\ \text{sec}})$	2.03×10^{-6}	1.42×10^{-6}	4.95×10^{-6}	3.45×10^{-6}
η	0.4409	0.3071	1.0729	0.7483
% DEV	--	30.3	--	30.3

$$\% \text{ DEV} = \frac{\eta_{DG} - \eta_{MDG}}{\eta_{DG}} \times 100$$

$C_o = 500 \times 10^{-12}$, $C_1 = 1000 \times 10^{-8}$, P = 1 atm

*Pellet Length = 1.1 cm

modified dusty-gas models, the percentage deviation between the two models is about the same when any of these parameters are varied in both models. It is the value of α and the pore-size distribution which determines the magnitude of difference between the two models, as shown by the results here and in Paper II and Paper III.

Additional numerical results giving the concentration and pressure profiles for the cases presented in this work may be obtained through the Chemical Engineering Department of the University of Missouri-Rolla.

APPENDIX C

COMPUTER PROGRAMS

A. INTRODUCTION

This appendix describes the five computer programs used to calculate the results given in this work. The programs were run on an AMDAHL 470/V8 computer, using FORTRAN IV language. The FORTRAN IV code is given for each program, along with a sample input and output data set. The first program, described in section A, shows the method used for computing the diffusion and slip-flow correction factors. The program described in Section B computes results predicted by the dusty-gas and modified dusty-gas models for binary isobaric diffusion. The program described in Section C computes the mass flux ratios, for a binary system of A and B, predicted by both models for simultaneous diffusion and flow. The program described in Section D uses these last results to compute the mass flux magnitudes for both components A and B for simultaneous diffusion and flow. The last program, described in Section E, computes results using both models for the case of chemical reactions with mole changes in a porous medium.

B. COMPUTER PROCEDURE FOR CORRECTION FACTOR DETERMINATION

The program described in this section computes the diffusion and slip-flow correction factors for the modified dusty-gas model as defined by Eqs. (13)-(15) in Paper I. The effectiveness function, $\Delta(R)$, and the pore-size volume distribution $V(R)$ are specified in subroutines in the program. The subroutine DELTAR provides the computer code which defines $\Delta(R)$ as given by Eq. (12) in Paper I. The code for $V(R)$ is given in two subroutines, VOFR1 and VOFR2. Since one analytic function may not be adequate to describe the pore-size volume distribution over the total range of pore radii, two subroutines are used to describe $V(R)$, with the subroutine VOFR1 providing the function which describes the volume distribution from R=0 to R=NR1, and the subroutine VOFR2 describing the volume distribution from R=NR1 to some specified maximum radius, NR2. The code for the functions defining the two pore-size volume distributions tested in this work are given in the program code at the end of this section.

The remaining subroutine in this program, PDIFF, provides a value for the pressure times the binary diffusivity, PD_{AB}, which is calculated from the following analytic expression, given in the text entitled "Transport Phenomena", published by John Wiley & Sons and authored by Bird, Stewart, and Lightfoot, p. 505 (1970):

$$PD_{AB} = 0.0002745(P_{c_A}P_{c_B})^{1/3}(T_{c_A}T_{c_B})^{5/12} \times \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}\left(\frac{T}{\sqrt{T_{c_A}T_{c_B}}}\right)^{1.823} \tag{1}$$

The parameters in Eqs. (13)-(15) in Paper I are evaluated over the range of pore sizes from R=0 to R=NR2=R_{max}, where NR2 is specified in the program input data. The summations are evaluated using Simpson's rule over the pore-size range. The diffusion and slip-flow correction factors are calculated at all values of pressure specified in the input data at each value of the parameter α specified.

The Fortran IV code for the program follows, along with a sample input data set and the resulting output.

```
C
C     *********************************************************
C     *                                                       *
C     *     THIS PROGRAM CALCULATES THE DIFFUSION AND         *
C     *     SLIP-FLOW CORRECTION FACTORS OVER A RANGE         *
C     *     OF PRESSURES FOR A BINARY SYSTEM OF COMPONENTS    *
C     *     A AND B FOR THE MODIFIED DUSTY-GAS MODEL.         *
C     *     THE FUNCTIONS DEFINING THE PORE-SIZE DISTRI-      *
C     *     BUTION AND THE EFFECTIVENESS FUNCTION  ARE        *
C     *     DESIGNATED IN THE SUBROUTINES.  VARIOUS           *
C     *     VALUES OF THE PARAMETER ALPHA MAY BE USED.        *
C     *                                                       *
C     *********************************************************
C
C
C                IDENTIFICATION OF VARIABLES AND ARRAYS
C
C            YAO = MOLE FRACTION OF COMPONENT A AT Z=0
C            YAL = MOLE FRACTION OF COMPONENT A AT Z=L
C            WMA = MOLECULAR WEIGHT OF A
C            WMB = MOLECULAR WEIGHT OF B
C             T  = TEMPERATURE OF THE SYSTEM (K)
C            TCA = CRITICAL TEMP OF COMPONENT A
C            TCB = CRITICAL TEMP OF COMPONENT B
C            PCA = CRITICAL PRESSURE OF COMPONENT A
C            PCB = CRITICAL PRESSURE OF COMPONENT B
C            NR1 = INTERMEDIATE PORE RADIUS WHERE V(R) CAN BE
C                  SEPARATED INTO TWO SEPARATE FUNCTION (ANGSTROMS)
C            NR2 = MAXIMUM PORE RADIUS (ANGSTROMS)
C             RM = THE VALUE OF THE MEAN RADIUS USING THE DEFINITION
C                  THAT EXCLUDES THE EFFECTIVNESS FUNCTION.
C
C        ALP(NA) = VECTOR OF NA VALUES OF THE PARAMETER ALPHA
C         PR(NP) = VECTOR OF NP VALUES OF THE PRESSURE
C       RADM(NA) = VECTOR OF THE VALUES OF THE MEAN PORE RADII
C                    AT THE 'NA' VALUES OF THE PARAMETER ALPHA USING
C                    THE DEFINITION FOR THE MEAN RADIUS THAT INCLUDES
C                    THE EFFECTIVENESS FUNCTION.
C     CDA(NP,NA) = ARRAY OF THE DIFFUSION CORRECTION FACTORS USING
C                  THE VALUES OF RADM(NA) FOR THE MEAN RADIUS AT THE
C                  NP VALUES OF PRESSURE AND NA VALUES OF ALPHA
C     CSA(NP,NA) = ARRAY OF THE SLIP-FLOW CORRECTION FACTORS FOR
C                  COMPONENT A USING THE VALUES OF RADM(NA) FOR
C                  THE MEAN RADIUS AT THE NP VALUES OF PRESSURE
```

```
C                 AND NA VALUES OF ALPHA.
C    CSB(NP,NA) = ARRAY OF THE SLIP-FLOW CORRECTION FACTORS FOR
C                 COMPONENT B USING THE VALUES OF RADM(NA) FOR
C                 THE MEAN RADIUS AT THE NP VALUES OF PRESSURE
C                 AND NA VALUES OF ALPHA.
C    PDA(NP,NA) = ARRAY OF THE DIFFUSION CORRECTION FACTORS USING
C                 THE VALUE OF RM FOR THE MEAN RADIUS AT THE
C                 NP VALUES OF PRESSURE AND NA VALUES OF ALPHA
C    PSA(NP,NA) = ARRAY OF THE SLIP-FLOW CORRECTION FACTORS FOR
C                 COMPONENT A USING THE VALUE OF RM FOR THE
C                 MEAN RADIUS AT THE NP VALUES OF PRESSURE
C                 AND NA VALUES OF ALPHA.
C    PSB(NP,NA) = ARRAY OF THE SLIP-FLOW CORRECTION FACTORS FOR
C                 COMPONENT B USING THE VALUE OF RM FOR THE
C                 MEAN RADIUS AT THE NP VALUES OF PRESSURE
C                 AND NA VALUES OF ALPHA.
C   DVC,DSA,DSB = THESE ARE ARRAYS WHICH CALCULATE THE DEVIATION
C                 BETWEEN CDA AND PDA, CSA AND PSA, AND CSB AND
C                 PSB, RESPECTIVELY.
C
C             THE REMAINING VECTORS ARE DUMMY VECTORS OR WORKING
C             VECTORS USED ONLY IN CALCULATING THE SUMMATIONS.
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION RNUM1(2000),RNUM2(2000),RDEN1(2000),RDEN2(2000)
      DIMENSION CDA1(200),CSA1(200),CSB1(200)
      DIMENSION RX(200),CD(200),RADM(7)
      DIMENSION CDA(200,7),CSA(200,7),CSB(200,7)
      DIMENSION CDAR(2000),CSAR(2000),CSBR(2000),CDAR2(2000)
      DIMENSION CSAR2(2000),CSBR2(2000),ALP(100),PR(200)
      DIMENSION RNUM3(1500),RNUM4(1500),RDEN3(1500),RDEN4(1500)
      DIMENSION PDA(200,6),PSA(200,6),PSB(200,6)
      DIMENSION DVC(200,6),DSA(200,6),DSB(200,6)
C
C
C       READ IN THE BINARY SYSTEM'S PHYSICAL CHARACTERISTICS
C       AND ECHO CHECK THEM
C
      READ(5,*)YAO,YAL,WMA,WMB,T,TCA,TCB,PCA,PCB,NR1,NR2
      WRITE(6,181)YAO,YAL
  181 FORMAT(//,20X,'YAO',30X,D14.6,/,20X,'YAL',30X,D14.6)
      WRITE(6,182)WMA,WMB
  182 FORMAT(/,20X,'M.W. OF A',24X,D14.6,/20X,'M.W. OF B',24X,D14.6)
```

```
      WRITE(6,183)T
  183 FORMAT(/20X,'TEMP (K)',25X,D14.6)
      WRITE(6,184)TCA,TCB
  184 FORMAT(/,20X,'TCA',30X,D14.6,/,20X,'TCB',30X,D14.6)
      WRITE(6,185)PCA,PCB
  185 FORMAT(/,20X,'PCA',30X,D14.6,/,20X,'PCB',30X,D14.6)
      WRITE(6,186)NR1,NR2
  186 FORMAT(/20X,'NR1',33X,I7,/20X,'NR2',33X,I7)
C
C        CALL THE SUBROUTINE PDIFF TO CALCULATE THE BINARY
C        DIFFUSIVITY TIMES THE PRESSURE USING THE ANALYTICAL
C        FORM GIVEN BY BIRD, STEWART, AND LIGHTFOOT, "TRANSPORT
C        PHENOMENA", 505 (1960).
C
      CALL PDIFF(TCA,TCB,PCA,PCB,WMA,WMB,T,PDAB)
C
      WRITE(6,1)
      WRITE(6,83)PDAB
   83 FORMAT(/40X,D14.6//)
    1 FORMAT(//,20X,'PRESSURE TIMES DIFFUSIVITY, ATM CM2/SEC  :')
C
C           READ IN THE PRESSURES AND VALUES OF THE PARAMETER
C           ALPHA FOR WHICH THE CORRECTION FACTORS ARE TO BE
C           CALCULATED
C
      READ(5,*)NP
      READ(5,*)(PR(I),I=1,NP)
      READ(5,*)NA
      READ(5,*)(ALP(I),I=1,NA)
C
C      CORRECTION FACTORS WILL BE CALCULATED FOR NA VALUES OF ALPHA
C
      DO 334 NNN=1,NA
      ALPHA=ALP(NNN)
C
C
C             INTEGRATE THE EQUATIONS FOR THE HETEROPOROSITY
C             CORRECTION FACTORS USING SIMPSON'S RULE.  TWO
C             INTERVALS ARE USED: FROM 0 - NR1, AND FROM
C             NR1 - NR2.  THE SAME FUNCTION OR DIFFERENT
C             FUNCTIONS MAY BE USED.  THE EFFECTIVE VOLUME-
C             MEAN RADIUS WILL BE CALCULATED ALONG WITH THE
C             TRANSPORT COEFFICIENTS AND THE SUMMATIONS GIVEN IN
C             THE DEFINITION OF THE CORRECTION COEFFICIENTS.
```

```
C         THE CORRECTION COEFFICIENTS WILL BE CALCULATED USING
C         TWO DIFFERENT DEFINITIONS FOR THE MEAN RADIUS; BOTH
C         WITH AND WITHOUT THE EFFECTIVENESS FUNCTION IN ITS
C         DEFINTION.
C
      NRN=NR1+500
C
C
C          SET THE INCREMENT FOR THE FIRST NUMERICAL INTEGRATION
C          OF SIMPSON'S RULE AT 50 ANGSTROMS.
C
      RNUM1(1)=0.0
      RNUM2(1)=0.0
      RNUM3(1)=0.0
      RNUM4(1)=0.0
      RDEN1(1)=0.0
      RDEN2(1)=0.0
      RDEN3(1)=0.0
      RDEN4(1)=0.0
C
      N=NR1/50
C
C        BEGIN THE NUMERICAL INTEGRATION FOR THE FIRST FUNCTION,
C        CALLING THE SUBROUTINES FOR V(R) AND DELTA(R).
C
      DO 2 IR=50,NR1,50
      NN=N+1
      J=IR/50 +1
C
C       THE SUBROUTINE VOFR1 SPECIFIES THE FUNCTIONAL FORM OF
C       THE V(R); IT IS VALID UP TO A PORE SIZE OF NR1
C
      CALL VOFR1(IR,VR1)
C
C      THESE NEXT THREE IF,THEN STATEMENTS ARE USED TO CIRCUMVENT
C      THE INABILITY OF THE COMPUTER TO HANDLE NUMBERS WHOSE EXPONENTS
C      EXCEED THE BOUNDS OF +78 OR -78.
C
      IF(ALPHA.GE.0.001)DELR=1.0
      IF(ALPHA.GE.0.001.AND.IR.LE.15000)CALL DELTAR(DELR,ALPHA,IR)
      IF(ALPHA.GE.0.001)GO TO 4444
C
C        THE SUBROUTINE DELTAR CALCULATES THE VALUE OF THE
C        EFFECTIVENESS FUNCTION FOR A SPECIFIED VALUE OF ALPHA
```

```
C          AT A PARTICULAR PORE RADIUS 'IR'.
C
      CALL DELTAR(DELR,ALPHA,IR)
 4444 CONTINUE
      RNUM1(J)=IR*VR1*DELR
      RDEN1(J)=VR1*DELR
      IF(NNN.EQ.1)RNUM3(J)=IR*VR1
      IF(NNN.EQ.1)RDEN3(J)=VR1
    2 CONTINUE
C
      SNUM1=RNUM1(1)
      SDEN1=RDEN1(1)
      SNUM3=RNUM3(1)
      SDEN3=RNUM3(1)
C
      DO 3 I=2,N,2
      SNUM1=SNUM1+4*RNUM1(I)
      SDEN1=SDEN1+4*RDEN1(I)
      IF(NNN.EQ.1)SNUM3=SNUM3+4*RNUM3(I)
      IF(NNN.EQ.1)SDEN3=SDEN3+4*RDEN3(I)
    3 CONTINUE
      M=N-1
      DO 4 I=3,M,2
      SNUM1=SNUM1+2*RNUM1(I)
      SDEN1=SDEN1+2*RDEN1(I)
      IF(NNN.EQ.1)SNUM3=SNUM3+2*RNUM3(I)
      IF(NNN.EQ.1)SDEN3=SDEN3+2*RDEN3(I)
    4 CONTINUE
      SNUM1=SNUM1+RNUM1(NN)
      SDEN1=SDEN1+RDEN1(NN)
      IF(NNN.EQ.1)SNUM3=SNUM3+RNUM3(NN)
      IF(NNN.EQ.1)SDEN3=SDEN3+RDEN3(NN)
      RMNUM1=(50./3.)*SNUM1
      RMDEN1=(50./3.)*SDEN1
      IF(NNN.EQ.1)RMNUM3=(50./3.)*SNUM3
      IF(NNN.EQ.1)RMDEN3=(50./3.)*SDEN3
C
C          THE COMPUTATIONS CONTINUE USING THE DEFINITION OF V(R)
C          VALID FOR THE PORE RANGE NR1-NR2.  THIS FUNCTION IS
C          GIVEN IN THE SUBROUTINE VOFR1
C
      N2=(NR2-NR1)/500
      DO 5 IR=NRN,NR2,500
      NN2=N2+1
```

```
      J=(IR-NR1)/500 +1
      CALL VOFR2(IR,VR2)
      IF(ALPHA.GE.0.001)DELR=1.0
      IF(ALPHA.GE.0.001.AND.IR.LE.15000)CALL DELTAR(DELR,ALPHA,IR)
      IF(ALPHA.GE.0.001)GO TO 4445
      CALL DELTAR(DELR,ALPHA,IR)
 4445 CONTINUE
      RNUM2(J)=IR*VR2*DELR
      RDEN2(J)=VR2*DELR
      IF(NNN.EQ.1)RNUM4(J)=IR*VR2
      IF(NNN.EQ.1)RDEN4(J)=VR2
    5 CONTINUE
C
      SNUM2=RNUM1(NN)+RNUM2(NN2)
      SDEN2=RDEN1(NN)+RDEN2(NN2)
      IF(NNN.EQ.1)SNUM4=RNUM3(NN)+RNUM4(NN2)
      IF(NNN.EQ.1)SDEN4=RDEN3(NN)+RDEN4(NN2)
C
      DO 6 I=2,N2,2
      SNUM2=SNUM2+4*RNUM2(I)
      SDEN2=SDEN2+4*RDEN2(I)
      IF(NNN.EQ.1)SNUM4=SNUM4+4*RNUM4(I)
      IF(NNN.EQ.1)SDEN4=SDEN4+4*RDEN4(I)
    6 CONTINUE
C
      M2=N2-1
C
      DO 7 I=3,M2,2
      SNUM2=SNUM2+2*RNUM2(I)
      SDEN2=SDEN2+2*RDEN2(I)
      IF(NNN.EQ.1)SNUM4=SNUM4+2*RNUM4(I)
      IF(NNN.EQ.1)SDEN4=SDEN4+2*RDEN4(I)
    7 CONTINUE
C
C
C
      RMNUM2=(500./3.)*SNUM2
      RMDEN2=(500./3.)*SDEN2
      IF(NNN.EQ.1)RMNUM4=(500./3.)*SNUM4
      IF(NNN.EQ.1)RMDEN4=(500./3.)*SDEN4
C
C         CALCULATE THE R MEAN VALUE
C
      RMNUMT=RMNUM1+RMNUM2
```

```
      RMDENT=RMDEN1+RMDEN2
      RMEAN=RMNUMT/RMDENT
      IF(NNN.EQ.1)RMN=RMNUM3+RMNUM4
      IF(NNN.EQ.1)RMD=RMDEN3+RMDEN4
      IF(NNN.EQ.1)RM=RMN/RMD
      RADM(NNN)=RMEAN
C
C
C
C           BEGIN CALCULATIONS ON THE CORRECTION FACTORS FOR
C           DIFFUSION AND SLIP FLOW.
C
C           CALCULATE THE KNUDSEN DIFFUSIVITIES
C           OF COMPONENTS A AND B
C
C
      YAVG=0.5*(YA0+YAL)
      PK=2.D-08/3.*(( 8.0*8.317D07*T / 3.141593)**0.5)
      PKM=PK*((1.-YAVG)/DSQRT(WMA)) +PK*YAVG/(DSQRT(WMB))
      PKA=PK/(WMA**0.5)
      PKB=PK/(WMB**0.5)
C
C   CALCULATE THE CORRECTION FACTORS AT 'NP' VALUES OF PRESSURE.
C
      DO 333 III=1,NP
      P=PR(III)
C
C       CALCULATE THE VALUES OF THE TRANSPORT COEFFICIENTS
C       AT THE MEAN RADIUS (WHICH IS EVALUATED BOTH WITH AND
C       WITHOUT THE EFFECTIVENESS FUNCTION IN ITS DEFINITION).
C
      DARM=PDAB*PKA*RMEAN/(PDAB+(PKM*RMEAN*P))
      DBRM=PDAB*PKB*RMEAN/(PDAB+(PKM*RMEAN*P))
      SARM=RMEAN*(PDAB+PKB*RMEAN*P)*PKA/(PDAB+(PKM*RMEAN*P))
      SBRM=RMEAN*(PDAB+PKA*RMEAN*P)*PKB/(PDAB+(PKM*RMEAN*P))
C
      DARN=PDAB*PKA*RM/(PDAB+(PKM*RM*P))
      DBRN=PDAB*PKB*RM/(PDAB+(PKM*RM*P))
      SARN=RM*(PDAB+PKB*RM*P)*PKA/(PDAB+(PKM*RM*P))
      SBRN=RM*(PDAB+PKA*RM*P)*PKB/(PDAB+(PKM*RM*P))
C
C
C
C            BEGIN CALCULATIONS ON THE VOLUME-AVERAGED DIFFUSION
```

```
C             AND SLIP-FLOW TRANSPORT COEFFICIENTS; I.E., CALCULATE
C             THE COEFFICIENTS AT EACH VALUE OF R AND SUM THEM UP.
C
C             AS BEFORE, NUMERICAL INTEGRATION ON TWO INTERVALS
C             WILL BE USED. (THIS IS ONLY IF THE CUMULATIVE VOLUME
C             CURVE NEEDS TO BE APPROXIMATED BY TWO CURVES.)
C             THE SAME TYPE OF COMPUTATIONS FOLLOW AS ABOVE EXCEPT
C             THAT THE SUMMATIONS OF THE TRANSPORT COEFFICIENTS
C             ARE BEING CALCULATED INSTEAD OF THE MEAN RADIUS.
C
      DO 10 IR=50,NR1,50
      J=IR/50 +1
      CALL VOFR1(IR,VR1)
      IF(ALPHA.GE.0.001)DELR=1.0
      IF(ALPHA.GE.0.001.AND.IR.LE.15000)CALL DELTAR(DELR,ALPHA,IR)
      IF(ALPHA.GE.0.001)GO TO 4446
      CALL DELTAR(DELR,ALPHA,IR)
 4446 CONTINUE
      CDAR(J)=PDAB*PKA*IR/(PDAB+(PKM*IR*P))*VR1*DELR
      CSAR(J)=PKA*IR*(PDAB+PKB*IR*P)/(PDAB+(PKM*IR*P))*VR1*DELR
      CSBR(J)=PKB*IR*(PDAB+PKA*IR*P)/(PDAB+(PKM*IR*P))*VR1*DELR
   10 CONTINUE
C
      SCDA=0.0
      SCSA=0.0
      SCSB=0.0
C
      DO 11 I=2,N,2
      SCDA=SCDA+4*CDAR(I)
      SCSA=SCSA+4*CSAR(I)
      SCSB=SCSB+4*CSBR(I)
   11 CONTINUE
C
      DO 12 I=3,M,2
      SCDA=SCDA+2*CDAR(I)
      SCSA=SCSA+2*CSAR(I)
      SCSB=SCSB+2*CSBR(I)
   12 CONTINUE
C
      SCDA1=(SCDA+CDAR(NN))*50./3.
      SCSA1=(SCSA+CSAR(NN))*50./3.
      SCSB1=(SCSB+CSBR(NN))*50./3.
C
C          CALCUATIONS CONTINUE BUT SWITCH TO THE SECOND
```

```
C          DEFINING FORM FOR V(R).
C
      DO 13 IR=NRN,NR2,500
      J=(IR-NR1)/500 + 1
      CALL VOFR2(IR,VR2)
      IF(ALPHA.GE.0.001)DELR=1.0
      IF(ALPHA.GE.0.001.AND.IR.LE.15000)CALL DELTAR(DELR,ALPHA,IR)
      IF(ALPHA.GE.0.001)GO TO 4447
      CALL DELTAR(DELR,ALPHA,IR)
 4447 CONTINUE
      CDAR2(J)=PDAB*PKA*IR/(PDAB+(PKM*IR*P))*VR2*DELR
      CSAR2(J)=PKA*IR*(PDAB+PKB*IR*P)/(PDAB+(PKM*IR*P))*VR2*DELR
      CSBR2(J)=PKB*IR*(PDAB+PKA*IR*P)/(PDAB+(PKM*IR*P))*VR2*DELR
   13 CONTINUE
C
      SCDA2=CDAR(NN)+CDAR2(NN2)
      SCSA2=CSAR(NN)+CSAR2(NN2)
      SCSB2=CSBR(NN)+CSBR2(NN2)
C
      DO 14 I=2,N2,2
      SCDA2=SCDA2+4*CDAR2(I)
      SCSA2=SCSA2+4*CSAR2(I)
      SCSB2=SCSB2+4*CSBR2(I)
   14 CONTINUE
C
      DO 15 I=3,M2,2
      SCDA2=SCDA2+2*CDAR2(I)
      SCSA2=SCSA2+2*CSAR2(I)
      SCSB2=SCSB2+2*CSBR2(I)
   15 CONTINUE
C
      SCDA2=(500./3.)*SCDA2
      SCSA2=(500./3.)*SCSA2
      SCSB2=(500./3.)*SCSB2
C
      SCDAT=SCDA1+SCDA2
      SCSAT=SCSA1+SCSA2
      SCSBT=SCSB1+SCSB2
C
C        CALCULATE THE CORRECTION FACTORS AT THE 'III' VALUE OF
C        PRESSURE AND THE 'NNN' VALUE OF ALPHA AND WRITE THEM OUT
C        FOR BOTH DEFINITIONS OF THE MEAN RADIUS.
C
      CDA(III,NNN)=SCDAT/(DARM*RMDENT)
```

```
      CSA(III,NNN)=SCSAT/(SARM*RMDENT)
      CSB(III,NNN)=SCSBT/(SBRM*RMDENT)
C
      PDA(III,NNN)=SCDAT/(DARN*RMDENT)
      PSA(III,NNN)=SCSAT/(SARN*RMDENT)
      PSB(III,NNN)=SCSBT/(SBRN*RMDENT)
C
C        CALCULATE THE PERCENTAGE DEVIATION BETWEEN THE CORRECTION
C        FACTORS EVALUATED AT THE TWO DIFFERENT VALUES OF THE
C        MEAN RADIUS.
C
      DVC(III,NNN)=(PDA(III,NNN)-CDA(III,NNN))/PDA(III,NNN)*100.
      DSA(III,NNN)=(PSA(III,NNN)-CSA(III,NNN))/PSA(III,NNN)*100.
      DSB(III,NNN)=(PSB(III,NNN)-CSB(III,NNN))/PSB(III,NNN)*100.
 333  CONTINUE
 334  CONTINUE
C
C          WRITE OUT THE VALUE OF ALPHA AND THE CORRESPONDING
C          VALUES OF THE TWO DIFFERENT MEAN PORE RADII.  SINCE
C          ONE DEFINITION DOES NOT CONTAIN THE PARAMETER ALPHA,
C           IT HAS ONLY ONE VALUE FOR ANY VALUE OF ALPHA.
C
      DO 688 I=1,NA
      WRITE(6,1129)ALP(I),RADM(I),RM
 1129 FORMAT(5X,'ALPHA',3X,D10.3,2X,'RMDR',2X,F10.3,2X,'RM',2X,F10.3)
 688  CONTINUE
      WRITE(6,1108)
 1108 FORMAT(///9X,'USING DELTA(R) IN DEFINITION FOR RMEAN')
C
C        WRITE OUT THE CORRECTION COEFFICIENTS AT THE VALUES
C        OF ALPHA AND PRESSURE SPECIFIED IN THE INPUT DATA.
C        THESE USE THE DEFINITON OF THE MEAN RADIUS WHICH
C        USES THE EFFECTIVENESS FUNCTION.
C
      WRITE(6,1110)
      DO 639 KK=1,NA
      DO 637 LL=1,NP
      WRITE(6,110)ALP(KK),PR(LL),CDA(LL,KK),CSA(LL,KK),
     %          CSB(LL,KK)
C
C      ONE MAY ALSO WRITE OUTPUT TO FILES '7' AND '8' IF DESIRED
C      BY REMOVING THE 'C' SPECIFYING THEM AS COMMENTS.
C
C     WRITE(7,110)ALP(KK),PR(LL),CDA(LL,KK),CSA(LL,KK),
```

```
C     %              CSB(LL,KK)
C      WRITE(8,110)ALP(KK),PR(LL),CDA(LL,KK),CSA(LL,KK),
C     %              CSB(LL,KK)
C
  637  CONTINUE
   639 CONTINUE
 1110  FORMAT(//,3X,'ALPHA',8X,'PRESSURE',10X,'PHID',
      % 9X,'PHISA',8X,'PHISB',/)
  110  FORMAT(1X,D10.3,2X,D13.6,3X,F11.7,2X,F11.7,2X,F11.7)
C
C
C         WRITE OUT THE CORRECTION COEFFICIENTS AT THE VALUES
C         OF ALPHA AND PRESSURE SPECIFIED IN THE INPUT DATA.
C         THESE USE THE DEFINITON OF THE MEAN RADIUS WHICH
C         DOES NOT USE THE EFFECTIVENESS FUNCTION, IF DESIRED.
C
C      WRITE(6,1109)
  1109 FORMAT(/,10X,'NOT USING DELTA(R) IN RMEAN DEF',/)
C      WRITE(6,1110)
       DO 139 KK=1,NA
       DO 137 LL=1,NP
C      WRITE(6,110)ALP(KK),PR(LL),PDA(LL,KK),PSA(LL,KK),
C     %              PSB(LL,KK)
C
  137  CONTINUE
  139  CONTINUE
C
C        WRITE OUT THE DEVIATIONS BETWEEN THE CORRECTION FACTORS
C        CALCULATED USING THE TWO DIFFERENT DEFINITIONS FOR THE
C        MEAN PORE RADIUS AT THE DIFFERENT VALUES OF ALPHA
C        AND PRESSURE, IF DESIRED.
C
C      WRITE(6,1130)
C1130  FORMAT(//,4X,'ALPHA',5X,'PRESSURE',5X,'DEVCD',7X,
C     % 'DEVSA',6X,'DEVSB',/)
C
       DO 977 I=1,NA
       DO 978 J=1,NP
C      WRITE(6,1002)ALP(I),PR(J),DVC(J,I),DSA(J,I),DSB(J,I)
  1002 FORMAT(1X,D10.3,1X,D11.4,1X,F10.6,1X,F11.6,1X,F11.6)
   978 CONTINUE
   977 CONTINUE
C
       STOP
```

```
      END
C
C              *********************
C              *    SUBROUTINES    *
C              *********************
C
C
C         SUBROUTINE TO COMPUTE THE FUNCTION DELTA(R)
C
      SUBROUTINE DELTAR(DELR,ALPHA,IR)
      IMPLICIT REAL*8(A-H,O-Z)
C
      R=IR*1.
      DELR=1.-DEXP(-1.*ALPHA*R)
      RETURN
      END
C
C        SUBROUTINE TO SPECIFY V(R); VALID UP TO A PORE SIZE OF NR1
C
      SUBROUTINE VOFR1(IR,VR1)
      IMPLICIT REAL*8(A-H,O-Z)
C
      A=0.3099861
      B= -1.307433
      C=IR*1.
      D=A*DLOG(C) +B
      E= -1.*D**2
      VR1=1.12838*DEXP(E)*A/C
      RETURN
      END
C
C     SUBROUTINE TO SPECIFY V(R) FROM R=NR1 TO R=NR2
C
      SUBROUTINE VOFR2(IR,VR2)
      IMPLICIT REAL*8(A-H,O-Z)
C
      VR2=0.02364/IR
      RETURN
      END
C
C       THE SUBROUTINE PDIFF CALCULATES THE BINARY
C       DIFFUSIVITY TIMES THE PRESSURE USING THE ANALYTICAL
C       FORM GIVEN BY BIRD, STEWART, AND LIGHTFOOT, "TRANSPORT
C       PHENOMENA", 505 (1960).
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```
C
      SUBROUTINE PDIFF(TCA,TCB,PCA,PCB,WMA,WMB,T,PDAB)
      IMPLICIT REAL*8(A-H,O-Z)
C
      A=0.0002745
      B=1.823
      C1=(PCA*PCB)**(1./3.)
      C2=(TCA*TCB)**(5./12.)
      C3=DSQRT((1./WMA) + (1./WMB))
      C4=T/((TCA*TCB)**0.5)
      PDAB=C1*C2*C3*A*(C4**B)
      RETURN
      END
C
C
      ************************************************************
      *                                                          *
      *                                                          *
      *  THESE TWO FOLLOWING SUBROUTINES SPECIFY THE PORE-SIZE   *
      *  DISTRIBUTION DESIGNATED AS V2(R) IN THE PUBLICATIONS,   *
      *  AND SHOULD BE SUBSTITUTED FOR SUBROUTINES VOFR1 AND     *
      *  VOFR2 ABOVE WHEN THE CORRECTION FACTORS FOR THIS        *
      *  PORE-SIZE DISTRIBUTION ARE DESIRED.                     *
      *                                                          *
      ************************************************************
C
C          ROUTINE TO SPECIFY V(R); VALID UP TO A PORE SIZE OF NR1
C
      SUBROUTINE VOFR1(IR,VR1)
      IMPLICIT REAL*8(A-H,O-Z)
C
      C=IR*1.
      G=0.7*DLOG10(C) -0.51
      G1= -1.0*G
      S2= (2.0/(DEXP(G) + DEXP(G1)))**2
      T=(DEXP(G)-DEXP(G1))/(DEXP(G)+DEXP(G1))
      TP=T**29
      VR1=(9.12*S2*TP)/C
      RETURN
      END
C
C         ROUTINE TO SPECIFY V(R) FROM R=NR1 TO R=NR2
C
      SUBROUTINE VOFR2(IR,VR2)
```

```
      IMPLICIT REAL*8(A-H,O-Z)
C
      C=IR*1.
      G=0.7*DLOG10(C) -0.51
      G1= -1.0*G
      S2= (2.0/(DEXP(G) + DEXP(G1)))**2
      T=(DEXP(G)-DEXP(G1))/(DEXP(G)+DEXP(G1))
      TP=T**29
      VR2=(9.12*S2*TP)/C
      RETURN
      END
```

```
             ***********************
             *  SAMPLE INPUT DATA  *
             ***********************

  0.02979
  0.96205
 28.013
  4.003
299.26
126.2
  5.19
 33.5
  2.24
  8000
600000
  1.0
  6.0
 10.0
 14.0
 20.0
      2
   1.D-02
   1.D-06
```

```
                 ******************************
                 *   SAMPLE OUTPUT RESULTS    *
                 ******************************

             YAO                                     0.297900D-01
             YAL                                     0.962050D+00

             M.W. OF A                               0.280130D+02
             M.W. OF B                               0.400300D+01

             TEMP (K)                                0.299260D+03

             TCA                                     0.126200D+03
             TCB                                     0.519000D+01

             PCA                                     0.335000D+02
             PCB                                     0.224000D+01

             NR1                                         8000
             NR2                                       600000

             PRESSURE TIMES DIFFUSIVITY, ATM CM2/SEC  :

                                0.8160650D+00


   ALPHA     0.100D-01  RMDR    13676.528   RM    10179.593
   ALPHA     0.100D-05  RMDR   272845.822   RM    10179.593


      USING DELTA(R) IN DEFINITION FOR RMEAN

  ALPHA        PRESSURE          PHID        PHISA        PHISB

 0.100D-01   0.100000D+01     0.3439471    1.0198979    0.9533158
 0.100D-01   0.600000D+01     0.5971293    1.0021558    0.9944956
 0.100D-01   0.100000D+02     0.6770210    1.0010419    0.9973197
 0.100D-01   0.140000D+02     0.7272186    1.0006298    0.9983745
```

```
0.100D-01    0.200000D+02      0.7767418    1.0003614    0.9990650
0.100D-05    0.100000D+01      0.9667983    1.0000539    0.9998606
0.100D-05    0.600000D+01      0.9878621    1.0000033    0.9999914
0.100D-05    0.100000D+02      0.9913471    1.0000014    0.9999963
0.100D-05    0.140000D+02      0.9931693    1.0000008    0.9999979
0.100D-05    0.200000D+02      0.9947480    1.0000004    0.9999989
```

C. COMPUTER PROCEDURE FOR BINARY ISOBARIC DIFFUSION

This program computes the mass fluxes predicted by the dusty-gas and modified dusty-gas models using Eq. (26) and Eq. (27) in Paper I. As specified in the input data, the mass fluxes are computed at the designated combinations of C_1, C_2, pressure and α for a particular pore-size distribution. The deviation of the mass flux predicted by the modified dusty-gas model from the mass flux predicted by the dusty-gas model is calculated and the values of the fluxes are printed.

With the value of the flux known for component A, the mole fraction of A can be calculated at a distance z along the pellet length from the following expression, obtained by rearranging Eq. (26) in Paper I and substituting z for the pellet length L:

$$y_A(z) = \frac{-1}{\theta_A}\left(1 - \theta_A y_{A_o} + \frac{C_2 D^o{}_{AB}}{K_A P}\right)\exp\left(\frac{N_A R_g T \theta_A z}{\phi_D C_2 D^o{}_{AB}}\right) + \frac{1}{\theta_A}\left(1 + \frac{C_2 D^o{}_{AB}}{K_A P}\right) \qquad (2)$$

The parameter θ_A is defined in Eq. (27) of Paper I. The mole fraction of A is calculated and printed at each of the NZ locations specified in the input data.

The only subroutine in this program, PDIFF, is used to calculate the pressure times the binary diffusivity and is described in Section A of this appendix. The annotated program listing follows, along with a sample input data set and the resulting output.

```
C     *************************************************************
C     *                                                           *
C     *   THIS PROGRAM CALCULATES THE MASS FLUXES, FOR A BINARY   *
C     *   SYSTEM OF A AND B, PREDICTED BY THE DUSTY-GAS AND THE   *
C     *   MODIFIED DUSTY-GAS MODELS FOR THE CASE OF ISOTHERMAL    *
C     *   BINARY ISOBARIC DIFFUSION.                              *
C     *                                                           *
C     *************************************************************
C
C
C              IDENTIFICATION OF INPUT VARIABLES AND ARRAYS
C
C          YAO = VALUE OF THE MOLE FRACTION OF A AT Z=0
C          YAL = VALUE OF THE MOLE FRACTION OF A AT Z=L
C          WMA = MOLECULAR WEIGHT OF COMPONENT A, G/GMOL
C          WMB = MOLECULAR WEIGHT OF COMPONENT B, G/GMOL
C           T  = TEMPERATURE OF SYSTEM, K
C          TCA = CRITICAL TEMPERATURE OF COMPONENT A, K
C          TCB = CRITICAL TEMPERATURE OF COMPONENT B, K
C          PCA = CRITICAL PRESSURE OF COMPONENT A, ATM
C          PCB = CRITICAL PRESSURE OF COMPOENT B, ATM
C         PLEN = PELLET LENGTH, CM
C          NC1 = NUMBER OF INPUT VALUES OF THE GEOMETRIC FACTOR C1
C          NC2 = NUMBER OF INPUT VALUES OF THE GEOMETRIC FACTOR C2
C           NP = NUMBER OF INPUT PRESSURE VALUES
C           NA = NUMBER OF INPUT VALUES OF THE PARAMETER 'ALPHA'
C           NZ = NUMBER OF PELLET LENGTH INCREMENTS FOR INTEGRATION
C
C      C1(NC1) = VECTOR OF NC1 VALUES OF THE PARAMETER C1
C      C2(NC2) = VECTOR OF NC2 VALUES OF THE PARAMETER C2
C        Z(NZ) = VECTOR OF NZ VALUES OF THE LENGTH INCREMENTS
C      ALP(NA) = VECTOR OF NA VALUES OF THE PARAMETER 'ALPHA'
C       PR(NP) = VECTOR OF NP VALUES OF THE PRESSURE
C   CD(NA,NP)  = ARRAY OF THE DIFFUSION CORRECTION FACTORS AT NA
C                VALUES OF 'ALPHA' AND NP VALUES OF THE PRESSURE
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION C1(25),C2(25),PR(25),ALP(25),Z(25),CD(25,25),YAZ(25)
C
C        THE COMPONENTS USED WERE NITROGEN AND HELIUM
C
      WRITE(6,796)
```

```
  796 FORMAT(//,9X,'COMPONENT A :',10X,'NITROGEN')
      WRITE(6,797)
  797 FORMAT(/,9X,'COMPONENT B :',10X,'HELIUM')
C
C       READ IN THE NECESSARY VALUES OF THE INPUT VARIABLES
C
      READ(5,*)YAO,YAL,WMA,WMB,T,TCA,TCB,PCA,PCB
      READ(5,*)PLEN
      READ(5,*)NC1,NC2,NP,NA,NZ
      READ(5,*)(C1(I),I=1,NC1)
      READ(5,*)(C2(I),I=1,NC2)
      READ(5,*)(Z(I),I=1,NZ)
C
      DO 499 KK=1,NA
      DO 499 LL=1,NP
      READ(5,593)ALP(KK),PR(LL),CD(KK,LL)
  593 FORMAT(1X,D10.3,2X,D13.6,3X,F11.7)
  499 CONTINUE
C
C      CALL THE SUBROUTINE 'PDIFF' TO CALCULATE THE VALUE
C      OF THE PRESSURE TIMES THE BINARY DIFFUSIVITY
C
      CALL PDIFF(TCA,TCB,PCA,PCB,WMA,WMB,T,PDAB)
C
C         WRITE OUT THE VALUES OF THE INPUT VARIABLES TO ECHO CHECK
C
      WRITE(6,881)YAO,YAL
  881 FORMAT(//,9X,'YAO',30X,D14.6,/9X,'YAL',30X,D14.6)
      WRITE(6,882)WMA,WMB
  882 FORMAT(/,9X,'M.W. OF A',24X,D14.6,/9X,'M.W. OF B',24X,D14.6)
      WRITE(6,883)T
  883 FORMAT(/9X,'TEMP (K)',25X,D14.6)
      WRITE(6,884)TCA,TCB
  884 FORMAT(/9X,'TCA',30X,D14.6,/,9X,'TCB',30X,D14.6)
      WRITE(6,885)PCA,PCB
  885 FORMAT(/,9X,'PCA',30X,D14.6,/,9X,'PCB',30X,D14.6)
      WRITE(6,890)PLEN
  890 FORMAT(/9X,'PELLET LENGTH',20X,D14.6)
      WRITE(6,887)
      WRITE(6,888)PDAB
  887 FORMAT(//,9X,'PRESSURE TIMES DIFFUSIVITY, ATM CM2/SEC  :')
  888 FORMAT(/35X,D15.8)
C
      GA=1.-DSQRT(WMA/WMB)
```

```
      GB=1.-DSQRT(WMB/WMA)
C
      WRITE(6,501)GA,GB
 501  FORMAT(//9X,'GA(=1-SQRT(WMA/WMB)',25X,D15.7,/,
     % 9X,'GB(=1.SQRT(WMB/WMA)',25X,D15.7)
C
C              BEGIN CALCULATIONS OF THE MASS FLUXES AT
C              THE VARIOUS COMBINATIONS OF THE PARAMETERS
C
      DO 30 L=1,NA
      DO 29 K=1,NP
      DO 28 J=1,NC2
      DO 27 I=1,NC1
C
C                  CALCULATE THE KNUDSEN DIFFUSIVITIES
C
      PKA=C1(I)*DSQRT(8.317D07*T/WMA)
      PKB=C1(I)*DSQRT(8.317D07*T/WMB)
C
C            THE CALCULATION OF THE MASS FLUX TERM IS
C            DIVIDED INTO PARTS.  THE ADDITION OF THE
C            LETTER 'A' AT THE END OF A VARIABLE NAME
C            SIGNIFIES A CALCULATION FOR COMPONENT A.
C
      COEFFA=PDAB/(82.057*T*GA)
      COEFFB=PDAB/(82.057*T*GB)
C
      FNUMA=1.0 -(GA*YAL)+C2(J)*PDAB/(PKA*PR(K))
      FDENA=1.0 -(GA*YAO)+C2(J)*PDAB/(PKA*PR(K))
C
      FNUMB=1.0-(GB*(1.-YAL))+C2(J)*PDAB/(PKB*PR(K))
      FDENB=1.0-(GB*(1.-YAO))+C2(J)*PDAB/(PKB*PR(K))
C
C        COMPUTE THE MASS FLUXES PREDICTED BY THE
C        MODIFIED DUSTY-GAS MODEL
C
      DNA=CD(L,K)*C2(J)*COEFFA/PLEN*DLOG(FNUMA/FDENA)
      DNB=CD(L,K)*C2(J)*COEFFB/PLEN*DLOG(FNUMB/FDENB)
C
C        COMPUTE THE MASS FLUXES PREDICTED
C        BY THE DUSTY-GAS MODEL
C
      C1NA=DNA/CD(L,K)
      C1NB=DNB/CD(L,K)
```

```
C
C           COMPUTE THE DEVIATION OF THE FLUX USING THE
C           CORRECTION COEFFICIENTS FROM THE FLUX WITHOUT
C           THE CORRECTION FACTOR
C
      ERRA=100.*(C1NA-DNA)/C1NA
      ERRB=100.*(C1NB-DNB)/C1NB
C
      GACALC=1.+DNB/DNA
C
C          CALCULATE THE VALUES OF THE MOLE FRACTION
C          OF COMPONENT A ALONG THE PELLET LENGTH
C
      DO 300 M=1,NZ
      X1=DNA/COEFFA*Z(M)/C2(J)/CD(L,K)
      X2=DEXP(X1)*FDENA -1.0-(C2(J)*PDAB/(PKA*PR(K)))
      YAZ(M)=-1.*X2/GA
 300  CONTINUE
C
C           WRITE OUT THE RESULTS
C
      WRITE(6,511)
  511 FORMAT(//3X,'ALPHA',2X,'PRESSURE',4X,'CD',6X,'C2',6X,'C1',
     % 10X,'NA',12X,'NB')
      WRITE(6,10)ALP(L),PR(K),CD(L,K),C2(J),C1(I),DNA,DNB
  10  FORMAT(1X,D8.1,1X,F6.2,3X,F8.6,2X,F4.2,1X,D9.2,2X,D12.5,2X,D12.5)
      WRITE(6,180)
 180  FORMAT(3X,'NA(CD=1)',6X,'NB(CD=1)',7X,'GACALC',
     % 4X,'DEV(A)',3X,'DEV(B)')
      WRITE(6,181)C1NA,C1NB,GACALC,ERRA,ERRB
 181  FORMAT(1X,D12.5,2X,D12.5,2X,F10.7,1X,F7.2,2X,F7.2/)
C
C     WRITE(6,511)
C 511 FORMAT(//2X,'ALPHA',2X,'PRESSURE',5X,'CD',6X,'C2',6X,'C1',
C    % 10X,'NA',12X,'NB',10X,'NA(C=1)',8X,'NB(C=1)',6X,'GACALC',
C    % 4X,'DEV(A)',3X,'DEV(B)',/)
C     WRITE(6,10)ALP(L),PR(K),CD(L,K),C2(J),C1(I),DNA,DNB,C1NA,
C    % C1NB,GACALC,ERRA,ERRB
C 10  FORMAT(D8.1,2X,F6.2,2X,F9.7,2X,F4.2,1X,D9.2,2X,D12.5,2X,D12.5,
C    % 2X,D12.5,2X,D12.5,2X,F10.7,1X,F7.2,2X,F7.2)
C
      WRITE(6,333)(Z(M),M=1,6)
  333 FORMAT(2X,'Z',3X,13F9.5)
      WRITE(6,334)(YAZ(M),M=1,6)
```

```
  334 FORMAT(1X,'YA',3X,13F9.5)
      WRITE(6,335)(Z(M),M=7,NZ)
  335 FORMAT(/6X,13F9.5)
      WRITE(6,336)(YAZ(M),M=7,NZ)
  336 FORMAT(6X,13F9.5)
   27 CONTINUE
   28 CONTINUE
   29 CONTINUE
   30 CONTINUE
C
C
      STOP
      END
C
C
C        THIS SUBROUTINE PDIFF TO CALCULATE THE BINARY
C        DIFFUSIVITY TIMES THE PRESSURE USING THE ANALYTICAL
C        FORM GIVEN BY BIRD, STEWART, AND LIGHTFOOT, "TRANSPORT
C        PHENOMENA", 505 (1960).
C
      SUBROUTINE PDIFF(TCA,TCB,PCA,PCB,WMA,WMB,T,PDAB)
      IMPLICIT REAL*8(A-H,O-Z)
C
      A=0.0002745
      B=1.823
      C1=(PCA*PCB)**(1./3.)
      C2=(TCA*TCB)**(5./12.)
      C3=DSQRT((1./WMA)+(1./WMB))
      C4=T/((TCA*TCB)**0.5)
      PDAB=C1*C2*C3*A*(C4**B)
      RETURN
      END
```

```
                    *********************
                    * SAMPLE INPUT DATA *
                    *********************
   0.02979
   0.96205
  28.013
   4.003
 299.26
 126.2
   5.19
  33.5
   2.24
   0.635
  1
  1
  5
  2
 13
1000.D-08
  0.8
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.635
0.100D-01    0.100000D+01     0.3439471
0.100D-01    0.600000D+01     0.5971293
0.100D-01    0.100000D+02     0.6770210
0.100D-01    0.140000D+02     0.7272186
0.100D-01    0.200000D+02     0.7767418
0.100D-05    0.100000D+01     0.9667983
0.100D-05    0.600000D+01     0.9878621
0.100D-05    0.100000D+02     0.9913471
0.100D-05    0.140000D+02     0.9931693
0.100D-05    0.200000D+02     0.9947480
```

```
               **************************
               * SAMPLE OUTPUT RESULTS *
               **************************

        COMPONENT A :          NITROGEN

        COMPONENT B :          HELIUM

        YAO                                     0.297900D-01
        YAL                                     0.962050D+00

        M.W. OF A                               0.280130D+02
        M.W. OF B                               0.400300D+01

        TEMP (K)                                0.299260D+03

        TCA                                     0.126200D+03
        TCB                                     0.519000D+01

        PCA                                     0.335000D+02
        PCB                                     0.224000D+01

        PELLET LENGTH                           0.635000D+00

        PRESSURE TIMES DIFFUSIVITY, ATM CM2/SEC  :

                                  0.81606498D+00


        GA(=1-SQRT(WMA/WMB)                                     -0.1645374D+01
        GB(=1.SQRT(WMB/WMA)                                      0.6219816D+00

    ALPHA  PRESSURE    CD       C2      C1           NA            NB
   0.1D-01   1.00   0.343947  0.80  0.10D-04  -0.33929D-05   0.89754D-05
    NA(CD=1)      NB(CD=1)       GACALC     DEV(A)    DEV(B)
  -0.98645D-05   0.26095D-04   -1.6453736   65.61     65.61

   Z      0.05000  0.10000  0.15000  0.20000  0.25000  0.30000
  YA      0.09081  0.15372  0.21859  0.28546  0.35441  0.42549
```

```
         0.35000  0.40000  0.45000  0.50000  0.55000  0.60000  0.63500
         0.49877  0.57433  0.65223  0.73255  0.81535  0.90072  0.96205

  ALPHA   PRESSURE     CD        C2        C1          NA              NB
 0.1D-01    6.00    0.597129   0.80   0.10D-04   -0.11163D-04    0.29529D-04
  NA(CD=1)        NB(CD=1)        GACALC      DEV(A)     DEV(B)
-0.18694D-04    0.49452D-04    -1.6453736    40.29      40.29

 Z       0.05000  0.10000  0.15000  0.20000  0.25000  0.30000
YA       0.08097  0.13520  0.19266  0.25354  0.31804  0.38639

         0.35000  0.40000  0.45000  0.50000  0.55000  0.60000  0.63500
         0.45880  0.53553  0.61683  0.70297  0.79424  0.89095  0.96205

  ALPHA   PRESSURE     CD        C2        C1          NA              NB
 0.1D-01   10.00    0.677021   0.80   0.10D-04   -0.13659D-04    0.36132D-04
  NA(CD=1)        NB(CD=1)        GACALC      DEV(A)     DEV(B)
-0.20174D-04    0.53369D-04    -1.6453736    32.30      32.30

 Z       0.05000  0.10000  0.15000  0.20000  0.25000  0.30000
YA       0.07944  0.13228  0.18853  0.24840  0.31213  0.37996

         0.35000  0.40000  0.45000  0.50000  0.55000  0.60000  0.63500
         0.45216  0.52902  0.61082  0.69790  0.79058  0.88923  0.96205

  ALPHA   PRESSURE     CD        C2        C1          NA              NB
 0.1D-01   14.00    0.727219   0.80   0.10D-04   -0.15190D-04    0.40183D-04
  NA(CD=1)        NB(CD=1)        GACALC      DEV(A)     DEV(B)
-0.20887D-04    0.55255D-04    -1.6453736    27.28      27.28

 Z       0.05000  0.10000  0.15000  0.20000  0.25000  0.30000
YA       0.07871  0.13089  0.18656  0.24595  0.30930  0.37688

         0.35000  0.40000  0.45000  0.50000  0.55000  0.60000  0.63500
         0.44897  0.52588  0.60792  0.69544  0.78880  0.88840  0.96205

  ALPHA   PRESSURE     CD        C2        C1          NA              NB
 0.1D-01   20.00    0.776742   0.80   0.10D-04   -0.16668D-04    0.44092D-04
  NA(CD=1)        NB(CD=1)        GACALC      DEV(A)     DEV(B)
-0.21458D-04    0.56765D-04    -1.6453736    22.33      22.33
```

```
  Z      0.05000  0.10000  0.15000  0.20000  0.25000  0.30000
 YA      0.07813  0.12979  0.18500  0.24400  0.30704  0.37442

         0.35000  0.40000  0.45000  0.50000  0.55000  0.60000  0.63500
         0.44642  0.52337  0.60560  0.69347  0.78738  0.88773  0.96205

   ALPHA   PRESSURE     CD        C2        C1           NA              NB
  0.1D-05    1.00    0.966798   0.80  0.10D-04  -0.95370D-05    0.25229D-04
   NA(CD=1)        NB(CD=1)         GACALC      DEV(A)    DEV(B)
 -0.98645D-05    0.26095D-04   -1.6453736     3.32      3.32

  Z      0.05000  0.10000  0.15000  0.20000  0.25000  0.30000
 YA      0.09081  0.15372  0.21859  0.28546  0.35441  0.42549

         0.35000  0.40000  0.45000  0.50000  0.55000  0.60000  0.63500
         0.49877  0.57433  0.65223  0.73255  0.81535  0.90072  0.96205

   ALPHA   PRESSURE     CD        C2        C1           NA              NB
  0.1D-05    6.00    0.987862   0.80  0.10D-04  -0.18467D-04    0.48852D-04
   NA(CD=1)        NB(CD=1)         GACALC      DEV(A)    DEV(B)
 -0.18694D-04    0.49452D-04   -1.6453736     1.21      1.21

  Z      0.05000  0.10000  0.15000  0.20000  0.25000  0.30000
 YA      0.08097  0.13520  0.19266  0.25354  0.31804  0.38639

         0.35000  0.40000  0.45000  0.50000  0.55000  0.60000  0.63500
         0.45880  0.53553  0.61683  0.70297  0.79424  0.89095  0.96205

   ALPHA   PRESSURE     CD        C2        C1           NA              NB
  0.1D-05   10.00    0.991347   0.80  0.10D-04  -0.20000D-04    0.52907D-04
   NA(CD=1)        NB(CD=1)         GACALC      DEV(A)    DEV(B)
 -0.20174D-04    0.53369D-04   -1.6453736     0.87      0.87

  Z      0.05000  0.10000  0.15000  0.20000  0.25000  0.30000
 YA      0.07944  0.13228  0.18853  0.24840  0.31213  0.37996

         0.35000  0.40000  0.45000  0.50000  0.55000  0.60000  0.63500
         0.45216  0.52902  0.61082  0.69790  0.79058  0.88923  0.96205
```

```
  ALPHA   PRESSURE     CD        C2       C1             NA             NB
 0.1D-05   14.00    0.993169   0.80   0.10D-04   -0.20745D-04    0.54878D-04
  NA(CD=1)          NB(CD=1)         GACALC      DEV(A)    DEV(B)
-0.20887D-04     0.55255D-04    -1.6453736      0.68      0.68

  Z       0.05000   0.10000   0.15000   0.20000   0.25000   0.30000
 YA       0.07871   0.13089   0.18656   0.24595   0.30930   0.37688

          0.35000   0.40000   0.45000   0.50000   0.55000   0.60000   0.63500
          0.44897   0.52588   0.60792   0.69544   0.78880   0.88840   0.96205

  ALPHA   PRESSURE     CD        C2       C1             NA             NB
 0.1D-05   20.00    0.994748   0.80   0.10D-04   -0.21346D-04    0.56467D-04
  NA(CD=1)          NB(CD=1)         GACALC      DEV(A)    DEV(B)
-0.21458D-04     0.56765D-04    -1.6453736      0.53      0.53

  Z       0.05000   0.10000   0.15000   0.20000   0.25000   0.30000
 YA       0.07813   0.12979   0.18500   0.24400   0.30704   0.37442

          0.35000   0.40000   0.45000   0.50000   0.55000   0.60000   0.63500
          0.44642   0.52337   0.60560   0.69347   0.78738   0.88773   0.96205
```

D. COMPUTER PROCEDURE FOR DETERMINING N_A/N_B FOR SIMULTANEOUS DIFFUSION AND FLOW

The flux ratio, N_A/N_B, is computed by the program described in this section for simultaneous diffusion and flow using Eq. (36) in Paper I and the subsequent procedure described there. The sixth-order Runge-Kutta integration routine utilized, DVERK, is an International Mathematical and Statistical Library, Inc. (IMSL) product, fully described and documented in the IMSL routine library, Edition 7, Version 8.1 (1979).

The subroutine FCN1 provides the Fortran IV code defining Eq. (36) in Paper I and is required by the integration routine DVERK. The remaining subroutine PL1 is a linear interpolation routine which provides values of the correction factors at required pressure values, using the inputted vectors of the correction factors.

The flux ratios are calculated at the designated combinations of C_0, C_1, C_2, ΔP, P_0, and α as specified by the input data. The results are printed out, with the output data set of this program designed as the input data set of the program described in the next section with no changes in format.

An annotated program listing, sample input data set and the resulting output follows.

```
C     ***********************************************************
C     *                                                         *
C     *   THIS PROGRAM CALCULATES THE FLUX RATIO, RAB=NA/NB, FOR *
C     *   THE CASE OF ISOTHERMAL SIMULTANEOUS DIFFUSION AND FLOW *
C     *   FOR A TWO-COMPONENT SYSTEM OF A AND B.  IT IS USED IN  *
C     *   CONJUNCTION WITH, AND PRECEDING, ANOTHER PROGRAM TO    *
C     *   DETERMINE THE VALUES OF THE FLUXES NA AND NB, AS WELL  *
C     *   AS THE CONCENTRATION AND PRESSURE PROFILES ALONG THE PEL- *
C     *   LET. RAB IS CALCULATED AT ONE VALUE OF ALPHA FOR VARIOUS *
C     *   COMBINATIONS OF CO,C1,C2, P, AND THE PRESSURE DROP.    *
C     *                                                         *
C     ***********************************************************
C
C               IDENTIFICATION OF INPUT VARIABLES AND ARRAYS
C
C            YAO = VALUE OF THE MOLE FRACTION OF A AT Z=0
C            YAL = VALUE OF THE MOLE FRACTION OF A AT Z=L
C            WMA = MOLECULAR WEIGHT OF COMPONENT A, G/GMOL
C            WMB = MOLECULAR WEIGHT OF COMPONENT B, G/GMOL
C             T  = TEMPERATURE OF SYSTEM, K
C          ALPHA = VALUE OF THE PARAMETER IN THE EFFECTIVENESS FUNCTION
C           PDAB = VALUE OF THE PRESSURE TIMES BINARY DIFFUSIVITY
C           PLEN = PELLET LENGTH, CM
C            NCO = NUMBER OF INPUT VALUES OF THE GEOMETRIC FACTOR CO
C            NC1 = NUMBER OF INPUT VALUES OF THE GEOMETRIC FACTOR C1
C            NC2 = NUMBER OF INPUT VALUES OF THE GEOMETRIC FACTOR C2
C             NP = NUMBER OF INPUT PRESSURE VALUES
C            NDP = NUMBER OF INPUT PRESSURE DROP VALUES
C
C        CO(NCO) = VECTOR OF NCO VALUES OF THE PARAMETER CO
C        C1(NC1) = VECTOR OF NC1 VALUES OF THE PARAMETER C1
C        C2(NC2) = VECTOR OF NC2 VALUES OF THE PARAMETER C2
C         PR(NP) = VECTOR OF NP VALUES OF THE PRESSURE
C      DELP(NDP) = VECTOR OF NDP VALUES OF THE PRESSURE DROP
C        CDF(64) = VECTOR OF 64 VALUES OF THE DIFFUSION CORRECTION
C                  FACTORS ENCOMPASSING THE PRESSURE RANGE INPUTTED.
C                  VECTOR WILL BE USED IN THE INTERPOLATING SUBROUTINE.
C         CA(64) = VECTOR OF 64 VALUES OF THE SLIP-FLOW CORRECTION
C                  FACTORS OF COMPONENT A ENCOMPASSING THE PRESSURE
C                  RANGE INPUTTED. VECTOR WILL BE USED IN THE
C                  INTERPOLATING SUBROUTINE.
C         CB(64) = VECTOR OF 64 VALUES OF THE SLIP-FLOW CORRECTION
C                  FACTORS OF COMPONENT B ENCOMPASSING THE PRESSURE
```

```
C                 RANGE INPUTTED. VECTOR WILL BE USED IN THE
C                 INTERPOLATING SUBROUTINE.
C
C              IDENTIFICATION OF OTHER VARIABLES AND ARRAYS
C
C         Y(1) = INDEPENDENT VARIABLE IN DERIVATIVE. REQUIRED FOR
C                INTEGRATION ROUTINE
C        C(24) = VECTOR REQUIRED FOR INTEGRATION ROUTINE
C       W(1,9) = WORKSPACE FOR INTEGRATION ROUTINE
C        Z(50) = VECTOR FOR VALUES OF Z ALONG PELLET LENGTH
C       YF(50) = VECTOR FOR MOLE FRACTIONS
C     CONC(50) = VECTOR OF MOLE FRACTION INCREMENTS USED IN
C                INTEGRATION ROUTINE
C         RAB  = DEFINES THE FLUX RATIO OF NA TO NB
C        KOUNT = NUMBER OF ITERATIONS TO FIND RAB
C          PS  = VALUE OF RELATIVE NORM
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION Y(1),C(24),W(1,9),CONC(15),PR(10),DELP(10)
      DIMENSION Z(50),YF(50),PRS(50)
      COMMON CO(15),C1(15),C2(15),DCO,DC1,DC2,PDAB,T,PKA,PKB
      COMMON RAB,UA,UB,WMA,WMB,DNA,DNB
      COMMON P(150),CDF(150),CA(150),CB(150)
      EXTERNAL FCN1
C
C          READ IN INPUT VALUES; ECHO CHECK
C
      READ(5,*) ALPHA
      READ(5,*)YAO,YAL,WMA,WMB,T
      READ(5,*)PDAB,PLEN
      WRITE(6,417)ALPHA,YAO,YAL,WMA,WMB,T
      WRITE(6,417)PDAB,PLEN
 417  FORMAT(10X,D14.7)
C
C          SET UP A INCREMENT VECTOR OF MOLE FRACTION GRID POINTS
C          ALONG WHICH TO INTEGRATE
C
      CONC(1)=YAO
      DE=(YAL-YAO)/10.
      DO 22 J=2,11
      JJ=J-1
      CONC(J)=CONC(JJ)+DE
 22   CONTINUE
```

```
C
C          CONTINUE TO READ INPUT VALUES; AGAIN ECHO CHECK
C
      READ(5,*)NCO,NC1,NC2,NP,NDP
      READ(5,*)(CO(I),I=1,NCO)
      READ(5,*)(C1(I),I=1,NC1)
      READ(5,*)(C2(I),I=1,NC2)
      READ(5,*)(PR(I),I=1,NP)
      READ(5,*)(DELP(I),I=1,NDP)
      WRITE(6,418)NCO,NC1,NC2,NP,NDP
 418  FORMAT(5X,I5)
      WRITE(6,417)(CO(I),I=1,NCO)
      WRITE(6,417)(C1(I),I=1,NC1)
      WRITE(6,417)(C2(I),I=1,NC2)
      WRITE(6,417)(PR(I),I=1,NP)
      WRITE(6,417)(DELP(I),I=1,NDP)
C
C           READ IN VALUES OF CORRECTION FACTORS (NOT FREE FORMAT)
C
      DO 433 IL=1,64
      READ(5,431)P(IL),CDF(IL),CA(IL),CB(IL)
      WRITE(6,431)P(IL),CDF(IL),CA(IL),CB(IL)
  431 FORMAT(13X,D13.6,3X,F11.7,2X,F11.7,2X,F11.7)
  433 CONTINUE
C
C         CALCULATE KNUDSEN DIFFUSIVITIES DIVIDED BY PARAMETER C1
C
      PKA=DSQRT(8.317D07*T/WMA)
      PKB=DSQRT(8.317D07*T/WMB)
C
C          SET UP LOOPS TO CALCULATE RAB AT DIFFERENT
C          COMBINATIONS OF THE VARIOUS PARAMETERS
C
      DO 32 IJ=1,NP
      DO 31 IK=1,NDP
      DO 30 I=1,NCO
      DO 29 J=1,NC1
      DO 28 K=1,NC2
C
      PFIN=PR(IJ)-DELP(IK)/760.
C
      RAB=+0.0001
      XL1=RAB
      KOUNT=0
```

```
      F3=0.0
      X3=0.0
  200 CONTINUE
C
C         NW,N,TOL,IND ARE VARIABLES FOR INTEGRATION ROUTINE
C
      NW=1
      N=1
      TOL=0.0005
      IND=1
      X=YAO
      Y(1)=PR(IJ)
      KOUNT=KOUNT+1
C
      DCO=CO(I)
      DC1=C1(J)
      DC2=C2(K)
C
C          INTEGRATE OVER THE 11 GRID POINTS FROM YAO TO YAL
C          USING THE IMSL ROUTINE DVERK, AS DESCRIBED IN THE
C          IMSL LIBRARY, EDITION 7, VERSION 8.1 (1979).  IT
C          IS A SIXTH-ORDER RUNGE-KUTTA INTEGRATION ROUTINE.
C
      DO 10 L=1,11
      XEND=CONC(L)
      CALL DVERK(N,FCN1,X,Y,XEND,TOL,IND,C,NW,W,IER)
      IF(IND.LT.0.OR.IER.GT.0)GO TO 20
   33 FORMAT(/5X,F10.4,10X,D15.7)
   10 CONTINUE
C
C         BEGIN ITERATION BY BISECTION METHOD TO CHECK
C         THE GUESSED VALUE OF RAB
C
      IF(KOUNT.EQ.1)RAB=-0.5
      IF(KOUNT.EQ.1)XR1=RAB
      IF(KOUNT.EQ.1)FL1=Y(1)-PFIN
      IF(KOUNT.EQ.1)GO TO 200
      IF(KOUNT.EQ.2)FR1=Y(1)-PFIN
      IF(KOUNT.EQ.2)RAB=(XL1*FR1-XR1*FL1)/(FR1-FL1)
      IF(KOUNT.EQ.2)GO TO 200
      X3=RAB
      F3=Y(1)-PFIN
      PS=DABS(F3/PFIN)
C
```

```
C          THE STOPPING CRITERIA ARE MEETING THE REQUIRED NORM
C          LEVEL GIVEN BY PS OR EXCEEDING THE 50 ITERATIONS
C
      IF(PS.LT.1.D-07)GO TO 105
      IF(KOUNT.GE.50)GO TO 104
C
      BL3=FL1*F3
      BR3=FR1*F3
      IF(BL3.GT.0)XL1=X3
      IF(BL3.GT.0)FL1=F3
      IF(BR3.GT.0)XR1=X3
      IF(BR3.GT.0)FR1=F3
C
C        PROVIDE ANOTHER STOPPING CRITERIA IF APPEARS THERE IS
C        NO SOLUTION IN GIVEN INTERVAL
C
      IF(BL3.GT.0.0.AND.BR3.GT.0.)GO TO 104
      BRL=FL1*FR1
      IF(BRL.GT.0.0)GO TO 104
      RAB=(XL1*FR1-XR1*FL1)/(FR1-FL1)
      GO TO 200
C
  105 CONTINUE
C
C        WRITE OUT THE CORRECT VALUE OF THE FLUX RATIO, THE NORM,
C        THE NUMBER OF ITERATIONS REQUIRED, AND THE INTEGER COUNTER
C        THE 'DO LOOPS' WERE ON (INDICATING VALUE OF THE PARAMETERS)
C
      WRITE(6,419)RAB,PS,KOUNT,IJ,IK,I,J,K
 419  FORMAT(7X,D15.7,4X,D11.4,3X,'KOUNT',2X,I5,I3,I3,I3,I3,I3)
C
      GO TO 28
C
 104  CONTINUE
      WRITE(6,116)RAB,KOUNT,IJ,IK,I,J,K
 116  FORMAT(/,2X,D15.7,3X,'KOUNT EXCEEDED',I5,3X,I3,I3,I3,I3,I3,/)
 28   CONTINUE
 29   CONTINUE
 30   CONTINUE
 31   CONTINUE
 32   CONTINUE
      STOP
 20   CONTINUE
      STOP
```

```
      END
C
C                 SUBROUTINES
C
C         THIS IS THE SUBROUTINE REQUIRED BY THE RUNGA-KUTTE
C         SIXTH-ORDER INTERGRATION ROUTINE TO DESCRIBE THE
C         DIFFERENTIAL EQUATION
C
      SUBROUTINE FCN1(N,X,Y,YPRIME)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION Y(1),C(24),W(1,9),YPRIME(N)
      COMMON C0(15),C1(15),C2(15),DC0,DC1,DC2,PDAB,T,PKA,PKB
      COMMON RAB,UA,UB,WMA,WMB,DNA,DNB
      COMMON P(150),CDF(150),CA(150),CB(150)
C
      PI=Y(1)
C                VALUES OF THE KNUDSEN DIFFUSIVITIES
      CKA=DC1*PKA
      CKB=DC1*PKB
      PKM=X*CKB +(1.-X)*CKA
C
C        CALCULATE VISCOSITY FOR THE MIXTURE
C
      UA=0.1418148D-06*Y(1) + 177.788D-06
      UB=196.1D-06
      UMN=(UA*X*DSQRT(WMA) +UB*(1.-X)*DSQRT(WMB))
      UMD=X*DSQRT(WMA)+(1.-X)*DSQRT(WMB)
      UM=UMN/UMD
C
C            FIND THE VALUE OF THE CORRECTION FACTORS AT THE
C            REQUIRED VALUE OF THE PRESSURE BY INTERPOLATING
C            BETWEEN THE VECTOR OF CORRECTION FACTOR VALUES
C            USING THE SUBROUTINE PL1.  (TO CALCULATE FOR THE
C            DUSTY-GAS MODEL, MAKE ALL CORRECTION FACTORS UNITY).
C
C     CALL PL1(PI,CD,CSA,CSB)
      CD=1.0
      CSA=1.0
      CSB=1.0
C
C          DEFINE HERE THE DIFFERENTIAL EQUATION
C
      ADEN= DC2*PDAB+PKM*Y(1)
      A= CD *DC2*PDAB*CKA*Y(1)/(ADEN*82.057*T)
```

```
      AP=CD *DC2*PDAB*CKB*Y(1)/(ADEN*82.057*T)
      B1=CSA *CKA*(DC2*PDAB+CKB*Y(1))/(ADEN)
      B=(B1+DC0*Y(1)*1.01325D06/UM) *X/(82.057*T)
C
      B2=CSB*CKB*(DC2*PDAB+CKA*Y(1))/ADEN
      BP=(B2+DC0*Y(1)*1.01325D06/UM)*(1.0-X)/(82.057*T)
C
C
      YPRIME(1)= -1.*(A+AP*RAB)/(B-BP*RAB)
C
      RETURN
      END
C
C       THIS SUBROUTINE LINEARLY INTERPOLATES BETWEEN THE
C       INPUTTED VALUES OF THE CORRECTION FACTORS TO GIVE
C       VALUES AT THE DESIRED PRESSURE, PI, AND RETURN THEM
C       TO THE INTEGRATION ROUTINE.
C
      SUBROUTINE PL1(PI,CD,CSA,CSB)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON C0(15),C1(15),C2(15),DC0,DC1,DC2,PDAB,T,PKA,PKB
      COMMON RAB,UA,UB,WMA,WMB,DNA,DNB
      COMMON P(150),CDF(150),CA(150),CB(150)
C
      IF(PI.GE.P(1).AND.PI.LE.P(16))GO TO 1
      IF(PI.GE.P(17).AND.PI.LE.P(32))GO TO 2
      IF(PI.GE.P(33).AND.PI.LE.P(48))GO TO 3
      IF(PI.GE.P(49).AND.PI.LE.P(64))GO TO 4
      CD=1.0
      CSA=1.0
      CSB=1.0
      GO TO 30
C
 1    CONTINUE
      DO 11 J=1,15
      JJ=J+1
      IF(PI.LE.P(JJ))CD=CDF(J)+(CDF(JJ)-CDF(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))CSA=CA(J)+(CA(JJ)-CA(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))CSB=CB(J)+(CB(JJ)-CB(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))GO TO 30
11    CONTINUE
 2    CONTINUE
      DO 12 J=17,31
      JJ=J+1
```

```
      IF(PI.LE.P(JJ))CD=CDF(J)+(CDF(JJ)-CDF(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))CSA=CA(J)+(CA(JJ)-CA(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))CSB=CB(J)+(CB(JJ)-CB(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))GO TO 30
   12 CONTINUE
    3 CONTINUE
      DO 13 J=33,47
      JJ=J+1
      IF(PI.LE.P(JJ))CD=CDF(J)+(CDF(JJ)-CDF(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))CSA=CA(J)+(CA(JJ)-CA(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))CSB=CB(J)+(CB(JJ)-CB(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))GO TO 30
   13 CONTINUE
    4 CONTINUE
      DO 14 J=49,63
      JJ=J+1
      IF(PI.LE.P(JJ))CD=CDF(J)+(CDF(JJ)-CDF(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))CSA=CA(J)+(CA(JJ)-CA(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))CSB=CB(J)+(CB(JJ)-CB(J))*(PI-P(J))/(P(JJ)-P(J))
      IF(PI.LE.P(JJ))GO TO 30
   14 CONTINUE
   30 CONTINUE
      RETURN
      END
```

```
                    **********************
                    * SAMPLE INPUT DATA *
                    **********************

1.D-06
0.02979,0.96205,28.013,4.003,299.26
 0.816065,0.635
  1,1,1,4,1
 25.D-12
 0.1000D-04
  0.45
  1.
  2.
  5.
 10.
 40.
 0.100D-05     0.850000D+00      0.9640858    1.0000685    0.9998229
 0.100D-05     0.860000D+00      0.9642859    1.0000673    0.9998259
 0.100D-05     0.870000D+00      0.9644829    1.0000662    0.9998288
 0.100D-05     0.880000D+00      0.9646770    1.0000651    0.9998317
 0.100D-05     0.890000D+00      0.9648681    1.0000640    0.9998345
 0.100D-05     0.900000D+00      0.9650565    1.0000630    0.9998372
 0.100D-05     0.910000D+00      0.9652420    1.0000620    0.9998398
 0.100D-05     0.920000D+00      0.9654249    1.0000610    0.9998423
 0.100D-05     0.930000D+00      0.9656051    1.0000600    0.9998448
 0.100D-05     0.940000D+00      0.9657828    1.0000591    0.9998473
 0.100D-05     0.950000D+00      0.9659580    1.0000581    0.9998496
 0.100D-05     0.960000D+00      0.9661307    1.0000572    0.9998519
 0.100D-05     0.970000D+00      0.9663010    1.0000564    0.9998542
 0.100D-05     0.980000D+00      0.9664690    1.0000555    0.9998564
 0.100D-05     0.990000D+00      0.9666348    1.0000547    0.9998585
 0.100D-05     0.100000D+01      0.9667983    1.0000539    0.9998606
 0.100D-05     0.185000D+01      0.9757816    1.0000213    0.9999448
 0.100D-05     0.186000D+01      0.9758516    1.0000211    0.9999453
 0.100D-05     0.187000D+01      0.9759212    1.0000209    0.9999457
 0.100D-05     0.188000D+01      0.9759902    1.0000208    0.9999461
 0.100D-05     0.189000D+01      0.9760587    1.0000206    0.9999466
 0.100D-05     0.190000D+01      0.9761267    1.0000204    0.9999470
 0.100D-05     0.191000D+01      0.9761943    1.0000203    0.9999474
 0.100D-05     0.192000D+01      0.9762613    1.0000201    0.9999479
 0.100D-05     0.193000D+01      0.9763279    1.0000199    0.9999483
 0.100D-05     0.194000D+01      0.9763939    1.0000198    0.9999487
 0.100D-05     0.195000D+01      0.9764595    1.0000196    0.9999491
```

```
0.100D-05   0.196000D+01   0.9765247   1.0000195   0.9999495
0.100D-05   0.197000D+01   0.9765894   1.0000193   0.9999499
0.100D-05   0.198000D+01   0.9766536   1.0000192   0.9999503
0.100D-05   0.199000D+01   0.9767173   1.0000190   0.9999506
0.100D-05   0.200000D+01   0.9767807   1.0000189   0.9999510
0.100D-05   0.485000D+01   0.9861231   1.0000047   0.9999879
0.100D-05   0.486000D+01   0.9861408   1.0000046   0.9999879
0.100D-05   0.487000D+01   0.9861584   1.0000046   0.9999880
0.100D-05   0.488000D+01   0.9861760   1.0000046   0.9999880
0.100D-05   0.489000D+01   0.9861936   1.0000046   0.9999881
0.100D-05   0.490000D+01   0.9862110   1.0000046   0.9999881
0.100D-05   0.491000D+01   0.9862285   1.0000046   0.9999881
0.100D-05   0.492000D+01   0.9862459   1.0000045   0.9999882
0.100D-05   0.493000D+01   0.9862632   1.0000045   0.9999882
0.100D-05   0.494000D+01   0.9862805   1.0000045   0.9999883
0.100D-05   0.495000D+01   0.9862977   1.0000045   0.9999883
0.100D-05   0.496000D+01   0.9863149   1.0000045   0.9999883
0.100D-05   0.497000D+01   0.9863320   1.0000045   0.9999884
0.100D-05   0.498000D+01   0.9863491   1.0000045   0.9999884
0.100D-05   0.499000D+01   0.9863661   1.0000044   0.9999884
0.100D-05   0.500000D+01   0.9863831   1.0000044   0.9999885
0.100D-05   0.985000D+01   0.9912570   1.0000014   0.9999962
0.100D-05   0.986000D+01   0.9912630   1.0000014   0.9999962
0.100D-05   0.987000D+01   0.9912691   1.0000014   0.9999963
0.100D-05   0.988000D+01   0.9912752   1.0000014   0.9999963
0.100D-05   0.989000D+01   0.9912812   1.0000014   0.9999963
0.100D-05   0.990000D+01   0.9912873   1.0000014   0.9999963
0.100D-05   0.991000D+01   0.9912933   1.0000014   0.9999963
0.100D-05   0.992000D+01   0.9912993   1.0000014   0.9999963
0.100D-05   0.993000D+01   0.9913053   1.0000014   0.9999963
0.100D-05   0.994000D+01   0.9913113   1.0000014   0.9999963
0.100D-05   0.995000D+01   0.9913173   1.0000014   0.9999963
0.100D-05   0.996000D+01   0.9913233   1.0000014   0.9999963
0.100D-05   0.997000D+01   0.9913293   1.0000014   0.9999963
0.100D-05   0.998000D+01   0.9913352   1.0000014   0.9999963
0.100D-05   0.999000D+01   0.9913412   1.0000014   0.9999963
0.100D-05   0.100000D+02   0.9913471   1.0000014   0.9999963
```

```
        **************************
        *  SAMPLE OUTPUT RESULTS *
        **************************
  0.1000000D-05
  0.2979000D-01
  0.9620500D+00
  0.2801300D+02
  0.4003000D+01
  0.2992600D+03
  0.8160650D+00
  0.6350000D+00
1
1
1
4
1
  0.2500000D-10
  0.1000000D-04
  0.4500000D+00
  0.1000000D+01
  0.2000000D+01
  0.5000000D+01
  0.1000000D+02
  0.4000000D+02
     0.850000D+00      0.9640858     1.0000685     0.9998229
     0.860000D+00      0.9642859     1.0000673     0.9998259
     0.870000D+00      0.9644829     1.0000662     0.9998288
     0.880000D+00      0.9646770     1.0000651     0.9998317
     0.890000D+00      0.9648681     1.0000640     0.9998345
     0.900000D+00      0.9650565     1.0000630     0.9998372
     0.910000D+00      0.9652420     1.0000620     0.9998398
     0.920000D+00      0.9654249     1.0000610     0.9998423
     0.930000D+00      0.9656051     1.0000600     0.9998448
     0.940000D+00      0.9657828     1.0000591     0.9998473
     0.950000D+00      0.9659580     1.0000581     0.9998496
     0.960000D+00      0.9661307     1.0000572     0.9998519
     0.970000D+00      0.9663010     1.0000564     0.9998542
     0.980000D+00      0.9664690     1.0000555     0.9998564
     0.990000D+00      0.9666348     1.0000547     0.9998585
     0.100000D+01      0.9667983     1.0000539     0.9998606
     0.185000D+01      0.9757816     1.0000213     0.9999448
     0.186000D+01      0.9758516     1.0000211     0.9999453
```

```
0.187000D+01        0.9759212        1.0000209        0.9999457
0.188000D+01        0.9759902        1.0000208        0.9999461
0.189000D+01        0.9760587        1.0000206        0.9999466
0.190000D+01        0.9761267        1.0000204        0.9999470
0.191000D+01        0.9761943        1.0000203        0.9999474
0.192000D+01        0.9762613        1.0000201        0.9999479
0.193000D+01        0.9763279        1.0000199        0.9999483
0.194000D+01        0.9763939        1.0000198        0.9999487
0.195000D+01        0.9764595        1.0000196        0.9999491
0.196000D+01        0.9765247        1.0000195        0.9999495
0.197000D+01        0.9765894        1.0000193        0.9999499
0.198000D+01        0.9766536        1.0000192        0.9999503
0.199000D+01        0.9767173        1.0000190        0.9999506
0.200000D+01        0.9767807        1.0000189        0.9999510
0.485000D+01        0.9861231        1.0000047        0.9999879
0.486000D+01        0.9861408        1.0000046        0.9999879
0.487000D+01        0.9861584        1.0000046        0.9999880
0.488000D+01        0.9861760        1.0000046        0.9999880
0.489000D+01        0.9861936        1.0000046        0.9999881
0.490000D+01        0.9862110        1.0000046        0.9999881
0.491000D+01        0.9862285        1.0000046        0.9999881
0.492000D+01        0.9862459        1.0000045        0.9999882
0.493000D+01        0.9862632        1.0000045        0.9999882
0.494000D+01        0.9862805        1.0000045        0.9999883
0.495000D+01        0.9862977        1.0000045        0.9999883
0.496000D+01        0.9863149        1.0000045        0.9999883
0.497000D+01        0.9863320        1.0000045        0.9999884
0.498000D+01        0.9863491        1.0000045        0.9999884
0.499000D+01        0.9863661        1.0000044        0.9999884
0.500000D+01        0.9863831        1.0000044        0.9999885
0.985000D+01        0.9912570        1.0000014        0.9999962
0.986000D+01        0.9912630        1.0000014        0.9999962
0.987000D+01        0.9912691        1.0000014        0.9999963
0.988000D+01        0.9912752        1.0000014        0.9999963
0.989000D+01        0.9912812        1.0000014        0.9999963
0.990000D+01        0.9912873        1.0000014        0.9999963
0.991000D+01        0.9912933        1.0000014        0.9999963
0.992000D+01        0.9912993        1.0000014        0.9999963
0.993000D+01        0.9913053        1.0000014        0.9999963
0.994000D+01        0.9913113        1.0000014        0.9999963
0.995000D+01        0.9913173        1.0000014        0.9999963
0.996000D+01        0.9913233        1.0000014        0.9999963
0.997000D+01        0.9913293        1.0000014        0.9999963
0.998000D+01        0.9913352        1.0000014        0.9999963
```

```
      0.999000D+01     0.9913412    1.0000014    0.9999963
      0.100000D+02     0.9913471    1.0000014    0.9999963
-0.3156663D+00     0.6546D-07   KOUNT     29  1  1  1  1  1
-0.3181327D+00     0.9877D-07   KOUNT     31  2  1  1  1  1
-0.3031454D+00     0.6416D-07   KOUNT     29  3  1  1  1  1
-0.2733289D+00     0.6711D-07   KOUNT     26  4  1  1  1  1
```

E. COMPUTER PROCEDURE FOR DETERMINING N_A AND N_B FOR SIMULTANEOUS DIFFUSION AND FLOW

Using the results from the preceding program, the mass fluxes, concentration profiles, and pressure profiles are calculated by the program described in this section for simultaneous diffusion and flow. Equations (28) and (29) in Paper I are numerically solved and described in the procedure following the equations. The procedure is essentially the same as used in the preceding program, with two differential equations now being simultaneously solved to yield the values of the mass fluxes for components A and B.

The subroutine FCN2 provides the code to describe the two differential equations to be solved. The subroutine PL1 is the same linear interpolation routine described in the preceding section.

The input data for this program are exactly the output data for the preceding program and the mass fluxes calculated are for the same combinations of the parameters C_0, C_1, C_2, ΔP, P_0, and α designated in that program. The solution of the differential equations for the case of simultaneous diffusion and flow was split into two separate programs solely for computational convenience.

The annotated program listing, along with the sample output set resulting from the input data provided by the preceding program, follow this section.

```
C      ****************************************************************
C      *                                                              *
C      *  THIS PROGRAM CALCULATES THE MAGNITUDE OF THE FLUXES         *
C      *  NA AND NB, ALONG WITH THE CONCENTRATION AND PRESSURE        *
C      *  PROFILES, FOR THE CASE OF ISOTHERMAL SIMULTANEOUS           *
C      *  DIFFUSION AND FLOW.  IT USES THE RATIO OF THE FLUXES,       *
C      *  NA/NB, AS DETERMINED BY A PRECEDING PROGRAM. THE INPUT      *
C      *  DATA FOR THIS PROGRAM IS SIMPLY THE OUTPUT FILE RESULTING   *
C      *  FROM THE PROGRAM WHICH CALCULATES THE VALUES OF THE FLUX    *
C      *  RATIO RAB.  THE TWO PROGRAMS MAY BE RUN CONSECUTIVELY       *
C      *  WITHOUT ANY DATA SET MANIPULATIONS.  THE FLUXES ARE         *
C      *  CALCULATED FOR ONE VALUE OF THE PARAMETER 'ALPHA' (THE      *
C      *  PARAMETER IN THE EFFECTIVENESS FUNCTION), AND AT THE        *
C      *  SAME COMBINATIONS OF THE PARAMETERS CO,C1,C2, PRESSURE,     *
C      *  AND THE PRESSURE DROP AS USED IN THE PROGRAM WHICH          *
C      *  CALCULATES THE FLUX RATIOS.                                 *
C      *                                                              *
C      ****************************************************************
C
C              IDENTIFICATION OF INPUT VARIABLES AND ARRAYS
C
C          YAO = VALUE OF THE MOLE FRACTION OF A AT Z=0
C          YAL = VALUE OF THE MOLE FRACTION OF A AT Z=L
C          WMA = MOLECULAR WEIGHT OF COMPONENT A, G/GMOL
C          WMB = MOLECULAR WEIGHT OF COMPONENT B, G/GMOL
C           T  = TEMPERATURE OF SYSTEM, K
C        ALPHA = VALUE OF THE PARAMETER IN THE EFFECTIVENESS FUNCTION
C         PDAB = VALUE OF THE PRESSURE TIMES BINARY DIFFUSIVITY
C         PLEN = PELLET LENGTH, CM
C          NCO = NUMBER OF INPUT VALUES OF THE GEOMETRIC FACTOR CO
C          NC1 = NUMBER OF INPUT VALUES OF THE GEOMETRIC FACTOR C1
C          NC2 = NUMBER OF INPUT VALUES OF THE GEOMETRIC FACTOR C2
C           NP = NUMBER OF INPUT PRESSURE VALUES
C          NDP = NUMBER OF INPUT PRESSURE DROP VALUES
C
C      CO(NCO) = VECTOR OF NCO VALUES OF THE PARAMETER CO
C      C1(NC1) = VECTOR OF NC1 VALUES OF THE PARAMETER C1
C      C2(NC2) = VECTOR OF NC2 VALUES OF THE PARAMETER C2
C       PR(NP) = VECTOR OF NP VALUES OF THE PRESSURE
C    DELP(NDP) = VECTOR OF NDP VALUES OF THE PRESSURE DROP
C        P(64) = VECTOR OF 64 VALUES OF PRESSURE AT WHICH THE
C                CORRECTION FACTORS HAVE BEEN EVALUATED
C      CDF(64) = VECTOR OF 64 VALUES OF THE DIFFUSION CORRECTION
```

```
C                FACTORS ENCOMPASSING THE PRESSURE RANGE INPUTTED.
C                VECTOR WILL BE USED IN THE INTERPOLATING SUBROUTINE.
C       CA(64) = VECTOR OF 64 VALUES OF THE SLIP-FLOW CORRECTION
C                FACTORS OF COMPONENT A ENCOMPASSING THE PRESSURE
C                RANGE INPUTTED. VECTOR WILL BE USED IN THE
C                INTERPOLATING SUBROUTINE.
C       CB(64) = VECTOR OF 64 VALUES OF THE SLIP-FLOW CORRECTION
C                FACTORS OF COMPONENT B ENCOMPASSING THE PRESSURE
C                RANGE INPUTTED. VECTOR WILL BE USED IN THE
C                INTERPOLATING SUBROUTINE.
C   RATIO(5,5,5,5,5)
C              =  ARRAY HOLDING THE VALUES OF THE FLUX RATIOS,RAB,
C                 AT THE VARIOUS COMBINATIONS OF THE PARAMETERS P,
C                 PRESSURE DROP, CO,C1, AND C2. (IF MORE THAN 5 VALUES
C                 OF A SINGLE PARAMETER IS TESTED, REDIMENSION ARRAY).
C
C              IDENTIFICATION OF OTHER VARIABLES AND ARRAYS
C
C         Y(2) = INDEPENDENT VARIABLES IN DERIVATIVES. REQUIRED FOR
C                INTEGRATION ROUTINE.
C        C(24) = VECTOR REQUIRED FOR INTEGRATION ROUTINE
C       W(2,9) = WORKSPACE FOR INTEGRATION ROUTINE
C        Z(50) = VECTOR FOR VALUES OF Z ALONG PELLET LENGTH
C       YF(50) = VECTOR FOR MOLE FRACTIONS
C     CONC(50) = VECTOR OF MOLE FRACTION INCREMENTS USED IN
C                INTEGRATION ROUTINE
C         RAB  = DEFINES THE FLUX RATIO OF NA TO NB
C        KOUNT = NUMBER OF ITERATIONS TO FIND RAB
C          PS  = VALUE OF RELATIVE NORM
C
C         DNA  = MAGNITUDE OF THE FLUX FOR COMPONENT A
C         DNB  = MAGNITUDE OF THE FLUX FOR COMPONENT B
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION Y(2),C(24),W(2,9),Z(50),PR(10),YF(50)
      DIMENSION DELP(10),PRS(50),RATIO(5,5,5,5,5)
      COMMON CO(15),C1(15),C2(15),DCO,DC1,DC2,PDAB,T,PKA,PKB
      COMMON RAB,UA,UB,WMA,WMB,DNA,DNB
      COMMON P(150),CDF(150),CA(150),CB(150)
      EXTERNAL FCN2
C
C
C          READ IN INPUT VALUES
```

```
C
      READ(5,*)ALPHA
      READ(5,*)YAO,YAL,WMA,WMB,T
      READ(5,*)PDAB
      READ(5,*)PLEN
C
C            CONSTRUCT A SERIES OF GRID POINTS ALONG THE PELLET
C            LENGTH OVER WHICH TO INTEGRATE NUMERICALLY
C
      Z(1)=0.0
      DE=PLEN/20.
      DO 22 J=2,21
      JJ=J-1
      Z(J)=Z(JJ)+DE
 22   CONTINUE
 120  FORMAT(10X,F9.5)
C
C            READ IN INPUT VALUES
C
      READ(5,*)NCO,NC1,NC2,NP,NDP
      READ(5,*)(CO(I),I=1,NCO)
      READ(5,*)(C1(I),I=1,NC1)
      READ(5,*)(C2(I),I=1,NC2)
      READ(5,*)(PR(I),I=1,NP)
      READ(5,*)(DELP(I),I=1,NDP)
      DO 1329 LI=1,64
      READ(5,1330)P(LI),CDF(LI),CA(LI),CB(LI)
 1330 FORMAT(13X,D10.3,3X,F10.6,2X,F11.7,2X,F10.6)
 1329 CONTINUE
C
C           SET UP LOOPS TO READ IN THE VARIOUS VALUES OF
C           THE FLUX RATIO, RAB
C
      DO 313 II=1,NP
      DO 313 JJ=1,NDP
      DO 313 I=1,NCO
      DO 313 J=1,NC1
      DO 313 K=1,NC2
C
C                 READ IN A VALUE OF THE FLUX RATIO, RAB
C
      READ(5,314)RATIO(II,JJ,I,J,K)
 314  FORMAT(7X,D15.7)
 313  CONTINUE
```

```
C
C          CALCULATE THE KNUDSEN DIFFUSIVITIES DIVIDED BY C1
C
      PKA=DSQRT(8.317D07*T/WMA)
      PKB=DSQRT(8.317D07*T/WMB)
C
C               SET UP LOOPS TO CALCULATE THE MASS FLUX
C               MAGNITUDES AT THE VARIOUS COMBINATIONS
C               OF THE PARAMETERS: PRESSURE, PRESSURE DROP,
C
C
      DO 32 IJ=1,NP
      DO 31 IK=1,NDP
      DO 30 I=1,NCO
      DO 29 J=1,NC1
      DO 28 K=1,NC2
C
      PFIN=PR(IJ)-DELP(IK)/760.
C
      RAB=RATIO(IJ,IK,I,J,K)
      DNA= -1.D-09
      R1=DNA
      KOUNT=0
  200 CONTINUE
C
C               TOL,NW,N, IND ARE PARAMETERS FOR THE INTEGRATION
C               ROUTINE DVERK.  SET UP ALSO THE INITIAL BOUNDARY
C               CONDITIONS HERE.
C
      X=0.0
      Y(1)=PR(IJ)
      Y(2)=YAO
      TOL=0.0001
      NW=2
      N=2
      IND=1
      KOUNT=KOUNT+1
C
      DCO=CO(I)
      DC1=C1(J)
      DC2=C2(K)
C
C             INTEGRATION PROCEDURE STARTS HERE OVER THE DESIGNATED
C             BOUNDARY CONDITIONS AT A GIVEN VALUE OF THE FLUX RATIO,
```

```
C              RAB, AND AT A GUESSED VALUE OF THE MAGNITUDE OF THE
C              FLUX NA.  THE IMSL ROUTINE DVERK, A SIXTH-ORDER RUNGE-
C              KUTTA INTEGRATION ROUTINE, IS USED.  DVERK IS DESCRIBED
C              IN DETAIL IN THE IMSL LIBRARY MANUALS, VERSION 8.1,
C              EDITION 7 (1979).
C
      DO 10 KK=1,21
      XEND=Z(KK)
      CALL DVERK(N,FCN2,X,Y,XEND,TOL,IND,C,NW,W,IER)
      IF(IND.LT.0.OR.IER.GT.0)GO TO 20
      PRS(KK)=Y(1)
      YF(KK)=Y(2)
   10 CONTINUE
C
C             A BISECTION METHOD IS USED TO DETERMINE A NEW GUESS
C             FOR THE FLUX NA
C
      IF(KOUNT.EQ.1)DNA=-1.D-03
      IF(KOUNT.EQ.1)P1=Y(1)
      IF(KOUNT.EQ.1)GO TO 200
      IF(KOUNT.EQ.2)R2=DNA
      IF(KOUNT.EQ.2)P2=Y(1)
      IF(KOUNT.EQ.2)DNA=0.5*(R1+R2)
      IF(KOUNT.EQ.2)GO TO 200
      R3=DNA
      P3=Y(1)
      A1=P1-PFIN
      A2=P2-PFIN
      A3=P3-PFIN
      B13=A1*A3
      B23=A2*A3
      IF(B13.LT.0)DNA=0.5*(R1+R3)
      IF(B13.LT.0)R2=R3
      IF(B13.LT.0)P2=P3
      IF(B23.LT.0)DNA=0.5*(R2+R3)
      IF(B23.LT.0)R1=R3
      IF(B23.LT.0)P1=P3
      PS=DABS(A3/PFIN)
      DNB=DNA/RAB
C
C             STOPPING CRITERIA ARE PROVIDED HERE. IF THE NUMBER OF
C             ITERATIONS EXCEED 50, STOP; IF THE RELATIVE NORM IS
C             AT AN ACCEPTABLE VALUE, STOP; OR, IF THERE DOESN'T
C             APPEAR TO BE A SOLUTION, STOP.
```

```
C
      IF(KOUNT.GE.50)GO TO 104
      IF(B13.GT.0.AND.B23.GT.0)GO TO 104
      IF(B13.LT.0.AND.B23.LT.0)GO TO 104
      IF(PS.LT.1.D-07) GO TO 105
      GO TO 200
C
C          WRITE OUT THE VALUES OF THE PARAMETERS, THE FLUX RATIO,
C          THE FLUX MAGNITUDES OF NA AND NB, AND THE CONCENTRATION
C          AND PRESSURE PROFILES ALONG THE PELLET LENGTH.
C
  105 CONTINUE
      WRITE(6,573)
 573  FORMAT(//3X,'ALPHA',8X,'C0',10X,'C1',6X,'C2',9X,'NA',14X,'NB')
      WRITE(6,574)ALPHA,DC0,DC1,DC2,DNA,DNB
 574  FORMAT(D10.3,1X,D10.3,2X,D10.3,2X,F4.2,2X,D14.7,2X,D14.7)
      WRITE(6,189)
      WRITE(6,188)RAB,DELP(IK),Z(1),PRS(1),YF(1)
 188  FORMAT(F10.6,1X,F5.1,2X,F7.5,2X,F9.6,2X,F8.6)
 189  FORMAT(/5X,'RAB',4X,'DP',7X,'Z',6X,'PRESSURE',5X,'YA')
      DO 575 JK=2,21
      WRITE(6,576)Z(JK),PRS(JK),YF(JK)
 576  FORMAT(18X,F7.5,2X,F9.6,2X,F8.6)
 575  CONTINUE
C
C
 28   CONTINUE
 29   CONTINUE
 30   CONTINUE
 31   CONTINUE
 32   CONTINUE
      STOP
  104 CONTINUE
      WRITE(6,116)KOUNT
  116 FORMAT(/5X,'KOUNT EXCEEDED',I5)
 20   CONTINUE
      STOP
      END
C
C                    SUBROUTINES
C
C
C          THE SUBROUTINE FCN2 DESCRIBES THE ORDINARY DIFFENTIAL
C          EQUATIONS TO BE SOLVED AND IS REQUIRED BY THE
```

```
C           INTEGRATION ROUTINE DVERK.
C
      SUBROUTINE FCN2(N,X,Y,YPRIME)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION Y(2),C(24),W(2,9),YPRIME(N)
      COMMON C0(15),C1(15),C2(15),DC0,DC1,DC2,PDAB,T,PKA,PKB
      COMMON RAB,UA,UB,WMA,WMB,DNA,DNB
      COMMON P(150),CDF(150),CA(150),CB(150)
C
      PI=Y(1)
C
C             CALCULATE KNUDSEN DIFFUSIVITIES
C
      CKA=DC1*PKA
      CKB=DC1*PKB
      PKM=Y(2)*CKB +(1.-Y(2))*CKA
C
C             CALCULATE THE VISCOSITY OF THE MIXTURE
C
      UA=0.1418148D-06*Y(1) + 177.788D-06
      UB=196.1D-06
      UMN=(UA*Y(2)*DSQRT(WMA)  +UB*(1.-Y(2))*DSQRT(WMB))
      UMD=Y(2)*DSQRT(WMA)+(1.-Y(2))*DSQRT(WMB)
      UM=UMN/UMD
C
C           CALL THE SUBROUTINE PL1 TO DETERMINE VALUES OF THE
C           CORRECTION FACTORS AT THE REQUIRED VALUE OF PRESSURE.
C
      CALL PL1(PI,CD,CSA,CSB)
C
C           DEFINE THE DIFFERENTIAL EQUATIONS. Y(1)IS PRESSURE AND
C           Y(2) IS THE MOLE FRACTION OF A.
C
      ADEN= DC2*PDAB+PKM*Y(1)
      A= CD *DC2*PDAB*CKA*Y(1)/(ADEN*82.057*T)
      AP=CD *DC2*PDAB*CKB*Y(1)/(ADEN*82.057*T)
      B1=CSA *CKA*(DC2*PDAB+CKB*Y(1))/(ADEN)
      B=(B1+DC0*Y(1)*1.01325D06/UM) *Y(2)/(82.057*T)
C
      B2=CSB*CKB*(DC2*PDAB+CKA*Y(1))/ADEN
      BP=(B2+DC0*Y(1)*1.01325D06/UM)*(1.-Y(2))/(82.057*T)
C
      DNB=DNA/RAB
C
```

```
      YPRIME(1)= -1.*(A*DNB+AP*DNA)/(A*BP+AP*B)
      YPRIME(2)= (B*DNB -BP*DNA)/(A*BP+AP*B)
C
      RETURN
      END
C
C          GIVEN A VECTOR OF VALUES OF THE CORRECTION FACTORS
C          AT GIVEN PRESSURES, SUBROUTINE PL1 LINEARLY INTERPOLATES
C          TO RETURN VALUES OF THE CORRECTION FACTORS TO THE
C          INTEGRATION PROCEDURE AT THE REQUIRED VALUE OF THE
C          PRESSURE.
C
      SUBROUTINE PL1(PI,CD,CSA,CSB)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON CO(15),C1(15),C2(15),DCO,DC1,DC2,PDAB,T,PKA,PKB
      COMMON RAB,UA,UB,WMA,WMB,DNA,DNB
      COMMON P(150),CDF(150),CA(150),CB(150)
C
      IF(PI.GE.P(1).AND.PI.LE.P(16))GO TO 1
      IF(PI.GE.P(17).AND.PI.LE.P(32))GO TO 2
      IF(PI.GE.P(33).AND.PI.LE.P(48))GO TO 3
      IF(PI.GE.P(49).AND.PI.LE.P(64))GO TO 4
      CD=1.0
      CSA=1.0
      CSB=1.0
      GO TO 30
C
  1   CONTINUE
      DO 11 J=1,15
      JJ=J+1
      IF(PI.LE.P(JJ))CD=CDF(J)+(CDF(JJ)-CDF(J))*(PI-P(J))/(P(JJ)-P(J))
 11   CONTINUE
      CSA=(CA(1) + CA(16))*0.5
      CSB=(CB(1) + CB(16))*0.5
      GO TO 30
  2   CONTINUE
      DO 12 J=17,31
      JJ=J+1
      IF(PI.LE.P(JJ))CD=CDF(J)+(CDF(JJ)-CDF(J))*(PI-P(J))/(P(JJ)-P(J))
 12   CONTINUE
      CSA=(CA(17)+ CA(32))*0.5
      CSB=(CB(17)+ CB(32))*0.5
      GO TO 30
  3   CONTINUE
```

```
      DO 13 J=33,47
      JJ=J+1
      IF(PI.LE.P(JJ))CD=CDF(J)+(CDF(JJ)-CDF(J))*(PI-P(J))/(P(JJ)-P(J))
13    CONTINUE
      CSA=(CA(33)+ CA(48))*0.5
      CSB=(CB(33)+ CB(48))*0.5
      GO TO 30
 4    CONTINUE
      DO 14 J=49,63
      JJ=J+1
      IF(PI.LE.P(JJ))CD=CDF(J)+(CDF(JJ)-CDF(J))*(PI-P(J))/(P(JJ)-P(J))
14    CONTINUE
      CSA=(CA(49)+ CA(64))*0.5
      CSB=(CB(49)+ CB(64))*0.5
      GO TO 30
30    CONTINUE
      RETURN
      END
```

```
                              *************************
                              * SAMPLE OUTPUT RESULTS *
                              *************************

   ALPHA          CO              C1        C2           NA                    NB
 0.100D-05   0.250D-10      0.100D-04   0.45   -0.6560738D-05      0.2078378D-04

    RAB       DP        Z          PRESSURE      YA
 -0.315666   40.0   0.00000      1.000000   0.029790
                    0.03175      0.997122   0.062486
                    0.06350      0.994268   0.096372
                    0.09525      0.991438   0.131490
                    0.12700      0.988632   0.167881
                    0.15875      0.985852   0.205586
                    0.19050      0.983097   0.244651
                    0.22225      0.980367   0.285119
                    0.25400      0.977663   0.327038
                    0.28575      0.974986   0.370455
                    0.31750      0.972336   0.415419
                    0.34925      0.969712   0.461981
                    0.38100      0.967116   0.510192
                    0.41275      0.964548   0.560108
                    0.44450      0.962008   0.611781
                    0.47625      0.959496   0.665271
                    0.50800      0.957012   0.720634
                    0.53975      0.954557   0.777931
                    0.57150      0.952132   0.837223
                    0.60325      0.949735   0.898576
                    0.63500      0.947368   0.962053

   ALPHA          CO              C1        C2           NA                    NB
 0.100D-05   0.250D-10      0.100D-04   0.45   -0.8406021D-05      0.2642300D-04

    RAB       DP        Z          PRESSURE      YA
 -0.318133   40.0   0.00000      2.000000   0.029790
                    0.03175      1.996946   0.060491
                    0.06350      1.993934   0.092495
                    0.09525      1.990964   0.125855
                    0.12700      1.988038   0.160626
                    0.15875      1.985155   0.196863
                    0.19050      1.982316   0.234626
                    0.22225      1.979522   0.273975
```

```
                              0.25400     1.976772   0.314974
                              0.28575     1.974068   0.357687
                              0.31750     1.971409   0.402183
                              0.34925     1.968796   0.448532
                              0.38100     1.966230   0.496806
                              0.41275     1.963709   0.547083
                              0.44450     1.961235   0.599440
                              0.47625     1.958807   0.653959
                              0.50800     1.956426   0.710724
                              0.53975     1.954092   0.769824
                              0.57150     1.951804   0.831350
                              0.60325     1.949563   0.895395
                              0.63500     1.947368   0.962059

   ALPHA          CO             C1        C2            NA                  NB
0.100D-05   0.250D-10     0.100D-04   0.45   -0.9770192D-05     0.3222939D-04

   RAB       DP         Z         PRESSURE       YA
-0.303145   40.0      0.00000     5.000000   0.029790
                      0.03175     4.996654   0.057822
                      0.06350     4.993383   0.087286
                      0.09525     4.990189   0.118252
                      0.12700     4.987072   0.150796
                      0.15875     4.984031   0.184993
                      0.19050     4.981067   0.220926
                      0.22225     4.978179   0.258679
                      0.25400     4.975368   0.298341
                      0.28575     4.972632   0.340005
                      0.31750     4.969972   0.383769
                      0.34925     4.967387   0.429735
                      0.38100     4.964877   0.478011
                      0.41275     4.962440   0.528709
                      0.44450     4.960076   0.581946
                      0.47625     4.957784   0.637847
                      0.50800     4.955563   0.696540
                      0.53975     4.953412   0.758161
                      0.57150     4.951330   0.822852
                      0.60325     4.949316   0.890763
                      0.63500     4.947369   0.962050

   ALPHA          CO             C1        C2            NA                  NB
0.100D-05   0.250D-10     0.100D-04   0.45   -0.9805001D-05     0.3587254D-04
```

```
     RAB        DP        Z          PRESSURE        YA
-0.273329     40.0    0.00000      10.000000     0.029790
                      0.03175       9.996452     0.055610
                      0.06350       9.993005     0.082949
                      0.09525       9.989658     0.111894
                      0.12700       9.986413     0.142537
                      0.15875       9.983267     0.174973
                      0.19050       9.980222     0.209306
                      0.22225       9.977275     0.245642
                      0.25400       9.974427     0.284096
                      0.28575       9.971675     0.324788
                      0.31750       9.969019     0.367845
                      0.34925       9.966458     0.413402
                      0.38100       9.963989     0.461599
                      0.41275       9.961612     0.512586
                      0.44450       9.959324     0.566522
                      0.47625       9.957124     0.623573
                      0.50800       9.955009     0.683917
                      0.53975       9.952979     0.747738
                      0.57150       9.951030     0.815236
                      0.60325       9.949160     0.886616
                      0.63500       9.947368     0.962101
```

F. COMPUTER PROCEDURE FOR REACTIONS WITH MOLE CHANGES

The program described in this section calculates the mass fluxes and effectiveness factors predicted by the dusty-gas and modified dusty-gas models for zero, first, and second-order irreversible reactions with mole changes in porous catalysts. The concentration and pressure profiles along the pellet length are calculated using Eqs. (9) and (10) in Paper II, with the boundary conditions given by Eqs. (12) and (13).

The program calculates discretization matrices of first and second order differential operators through the routines JCOBI and DISCRT. The application of these discretization matrices to the nonlinear ordinary differential equations through the procedure of orthogonal collocation yields the set of nonlinear algebraic equations specified in Eqs. (15) and (16) in Paper II. The orthogonal collocation procedure and a detailed description of the routines JCOBI and DISCRT are given by Villadsen and Michelsen (39).

The resulting set of algebraic equations are solved simultaneously using the International Mathematical and Statistical Library (IMSL) routine, ZSYSTM, described in detail in the IMSL manual, Edition 7, Version 8.1 (1979). The subroutine AUX defines the algebraic equations which are solved by the ZSYSTM routine, a Newton-like method based on Guassian elimination.

With the set of algebraic equations solved to provide the concentration and pressure profiles, the results are then used to calculate the values of the mass fluxes and reaction rates by using the subroutine EFF. Using the returned results from the subroutine EFF, the effectiveness factor, defined by Eq. (19) in Paper II, is calculated, with the integral in that equation evaluated using the subroutine INTEGR.

The dusty-gas model ($\phi_D=\phi_{SA}=\phi_{SB}=1.0$) is first used in determining, through an interative process, a rate constant which yields a value of $y_A \cong 0$ for some specified length $X_0 (0 \leq X_0 \leq 1)$. With this value of the rate constant, results for the modified dusty-gas model are calculated by determining the value of X_0, again through an iterative process, which yields a value of $y_A \cong 0$. A value of X_0 or the rate constant was assumed correct when a concentration profile resulted in which all boundary conditions were satisfied and the values of the mole fractions of A were less than 0.01 over approximately the last 25% of the pellet length.

The iterative process consists of first calculating the concentration and pressure profiles for values of the rate constant (or X_0) to be tested, as specified in the input data, and then analyzing the profiles for convergence to the correct solution. If, throughout the range of values of the rate constant (or X_0) tested, none of the resulting concentration profiles converges to a monotonically and continuously decreasing profile, a new range of input values should be tested. If there is a resulting concentration profile which decreases monotonically from a mole fraction of unity for component A to a value of y_A greater than zero at the designated value of X_0, the corresponding value of the rate constant (or X_0) should be increased until a concentration profile and pressure profile results which satisfy the boundary conditions and the error criteria previously specified. Since the solution procedure for solving the set of equations appears to have areas of local divergence, for a tested area of values of the rate constant (or X_0) there may be profiles which are divergent and convergent in the same range of values. If a monotonically decreasing concentration profile is found, the divergent profiles may be disregarded. It should be noted that the rapidity of convergence to the correct solution, as well as the area of convergence, depends to a large extent upon the accuracy of the initial estimates for the concentration and pressure profiles, which must be supplied for the ZSYSTM routine in the input data. This is especially true as the reaction order increases. When a correct solution is found, the program provides for calculating the corresponding mass fluxes, reaction rates, and the effectiveness factor.

An annotated program listing, input data set, and the resulting output follow.

```
C
C        *******************************************************
C        *                                                     *
C        *   THIS PROGRAM CALCULATES MASS FLUXES, EFFECTIVENESS *
C        *   FACTORS, AND CONCENTRATION AND PRESSURE PROFILES  *
C        *   FOR A GASEOUS CHEMICAL REACTION WITH MOLE CHANGES *
C        *   IN A HETEROPOROUS CATALYTIC PELLET, USING BOTH THE *
C        *   DUSTY-GAS AND MODIFIED DUSTY-GAS MODELS.   THE    *
C        *   METHOD OF ORTHOGONAL COLLOCATION TRANSFORMS THE   *
C        *   ORDINARY DIFFERENTIAL MATERIAL BALANCE EQUATIONS  *
C        *   INTO A SYSTEM OF ALGEBRAIC EQUATIONS, WHICH ARE   *
C        *   SOLVED BY AN QUADRATICALLY CONVERGENT NEWTON-LIKE *
C        *   METHOD BASED ON GAUSSIAN ELIMINATION.             *
C        *                                                     *
C        *******************************************************
C
C
C              IDENTIFICATION OF VARIABLES AND ARRAYS
C
C          WMA = MOLECULAR WEIGHT OF COMPONENT A, G/GMOL
C          WMB = MOLECULAR WEIGHT OF COMPONENT B, G/GMOL
C          YAO = VALUE OF THE MOLE FRACTION OF A AT Z=0
C           PO = VALUE OF THE PRESSURE AT Z=0
C           XO = VALUE OF THE PELLET LENGTH WHERE YA=0
C           T  = TEMPERATURE OF SYSTEM, K
C         PDAB = VALUE OF THE PRESSURE TIMES BINARY DIFFUSIVITY
C         PLEN = PELLET LENGTH, CM
C           CO = VALUE OF THE GEOMETRIC FACTOR CO, CM2
C           C1 = VALUE OF THE GEOMETRIC FACTOR C1, CM
C           C2 = VALUE OF THE GEOMETRIC FACTOR C2
C        RATEK = VALUE OF A RATE CONSTANT
C        THETA = STOCHIOMETRIC NUMBER IN IRREVERSIBLE REACTION
C           NC = NUMBER OF INTERNAL COLLOCATION POINTS
C           N  = NUMBER OF EQUATIONS TO BE SOLVED
C       NORDER = ORDER OF REACTION
C         NINT = NUMBER OF CORRECTION FACTOR VALUES READ IN
C         EPS  = NORM REQUIREMENT IN ROUTINE ZSYSTM
C         NSIG = NUMBER OF SIGNIFICANT DIGITS REQUIRED IN ZSYSTM
C        ITMAX = NUMBER OF ITERATIONS IN ZSYSTM
C        IFEFF = INPUT PARAMETER DETERMINING IN ONLY THE SOLUTION
C                CONCENTRATION AND PRESSURE PROFILES SHOULD BE
C                CALCULATED (IFEFF=0) OF IF CALCULATION OF MASS
C                FLUXES, REACTION RATES, AND EFFECTIVENESS FACTOR
C                (FOR THE LAST ITERATED COMBINATION OF RATE CONSTANT
```

```
C              AND XO) SHOULD PROCEED ('IFEFF' IS NON-ZERO).
C      BC1-4 = THE VALUES OF THE FOUR BOUNDARY CONDITIONS
C
C      X(50) = VECTOR CONTAINING THE PROFILE OF THE INDEPENDENT
C              VARIABLES, YA AND P, AT THE COLLOCATION GRID POINTS.
C   WA(3000) = WORKSPACE VECTORFOR ZSYSTM ROUTINE
C   PAR(100) = VECTOR PASSED IN ROUTINE ZSYSTM
C     YX(50) = VECTOR OF INITIAL PROFILES OF YA AND P
C   ALP(500) = VECTOR OF THE VALUE OF ALPHA ASSOCIATED WITH THE
C              INPUTTED CORRECTION FACTORS
C   CDF(500) = VECTOR OF INPUTTED DIFFUSION CORRECTION FACTORS
C    CA(500) = VECTOR OF INPUTTED SLIP-FLOW CORRECTION FACTORS FOR A
C    CB(500) = VECTOR OF INPUTTED DIFFUSION CORRECTION FACTORS FOR B
C     P(500) = VECTOR OF PRESSURES ASSOCIATED WITH THE CORRECTION
C              FACTORS
C     ZL(50) = VECTOR OF POINTS ALONG PELLET LENGTH
C     XW(50) = WORKSPACE VECTOR OF INDEPENDENT VARIABLES
C  RXNUM(50) = VECTOR OF SCALED REACTION RATESALONG PELLET LENGTH
C    DNA(50) = MASS FLUX VECTOR ALONG PELLET LENGTH FOR  A
C    DNB(50) = MASS FLUX VECTOR ALONG PELLET LENGTH FOR  B
C  RATIO(50) = RATIO OF MASS FLUX OF A TO MASS FLUX OF B
C   DIF1(50) = WORKSPACE VECTOR FOR OTHOGONAL COLLOCATION ROUTINES
C   DIF2(50) = WORKSPACE VECTOR FOR OTHOGONAL COLLOCATION ROUTINES
C   DIF3(50) = WORKSPACE VECTOR FOR OTHOGONAL COLLOCATION ROUTINES
C   DIF4(50) = WORKSPACE VECTOR FOR OTHOGONAL COLLOCATION ROUTINES
C   DIF5(50) = WORKSPACE VECTOR FOR OTHOGONAL COLLOCATION ROUTINES
C   ROOT(50) = VECTOR OF ORTHOGONAL COLLOCATION GRID POINTS
C   A(50,50) = ORTHOGONAL COLLOCATION DISCRETIZATION ARRAY FOR
C              THE FIRST DERIVATIVE
C   B(50,50) = ORTHOGONAL COLLOCATION DISCRETIZATION ARRAY FOR
C              THE SECOND DERIVATIVE
C
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(50),WA(3000),PAR(100),YX(50),ALP(500),ZL(50)
      DIMENSION XW(50),RXNUM(50),DNA(50),DNB(50),RATIO(50)
      DIMENSION DIF1(50),DIF2(50),DIF3(50),DIF4(50),DIF5(50),ROOT(50)
      DIMENSION XLENGTH(100),XCONST(100)
      COMMON /Q2/ A(50,50),B(50,50),P(500),CDF(500),CA(500),CB(500)
      COMMON /Q3/ WMA,WMB,T,PO,XO,YAO,PDAB,PLEN,CO,C1,C2,RATEK,THETA
      COMMON /Q3A/ YN2,PN2,BC3,BC4,UA,UB
      COMMON /Q4/ NC,N,NORDER,NC2,NC1,NINT
      EXTERNAL AUX
```

```
C
C
C            READ IN STOPPING CRITERIA FOR THE ROUTINE ZSYSTM
C            WHICH SOLVES THE SYSTEM OF ALGEBRAIC EQUATIONS.
C
      READ(5,*)EPS,NSIG,ITMAX
      CITMAX=ITMAX
C
C
C            READ IN THE NUMBER OF INTERNAL COLLOCATION POINTS,
C            NC, AND THE INITIAL GUESSED CONCENTRATION AND
C            PRESSURE PROFILES.
C
      READ(5,*)NC
      N=2*NC
      NC1=NC+1
      NC2=NC+2
      READ(5,*)(X(KL),KL=1,NC)
      READ(5,*)(X(KL),KL=NC1,N)
      DO 1311 JJ=1,N
      YX(JJ)=X(JJ)
 1311 CONTINUE
C
C          READ IN ALL OF THE VARIABLES DEFINING THE PHYSICAL
C          CHARACTERISTICS OF THE SYSTEM
C
      READ(5,*)NORDER,IFEFF
      READ(5,*)WMA,WMB,T,PLEN
      READ(5,*)YAO,PO
      READ(5,*)CO,C1,C2
      READ(5,*)TCA,TCB,PCA,PCB,UA,UB
C
      THETA=WMA/WMB
C
C             CALL SUBROUTINE PDIFF TO CALCULATE THE
C             BINARY DIFFUSIVITY TIMES PRESSURE.
C
      CALL PDIFF(TCA,TCB,PCA,PCB,WMA,WMB,T,PDAB)
C
C             WRITE OUT THE VALUES DEFINING THE PHYSICAL
C             PARAMETERS OF THE SYSTEM.
C
      WRITE(6,606)NORDER
  606 FORMAT(14X,'ORDER OF REACTION:',4X,I4/)
      WRITE(6,607)WMA,WMB
```

```
607   FORMAT(10X,'MOLECULAR WEIGHT OF A ',4X,F7.3/,10X,
     % 'MOLECULAR WEIGHT OF B ',4X,F7.3/)
      WRITE(6,612)THETA
612   FORMAT(8X,'THETA=MOL WT A/MOL WT B:',4X,F7.4/)
      WRITE(6,614)
614   FORMAT(13X,'THE GEOMETRIC PARAMETERS OF THE PELLET',/)
      WRITE(6,615)
615   FORMAT(18X,'C0',11X,'C1',11X,'C2',/)
      WRITE(6,616)C0,C1,C2
616   FORMAT(14X,D10.3,3X,D10.3,3X,D10.3/)
      WRITE(6,608)PDAB
609   FORMAT(25X,'INITIAL PROFILE')
      WRITE(6,609)
      WRITE(6,610)
610   FORMAT(/20X,'YA',20X,' P',/)
      WRITE(6,611)(X(K),X(K+NC),K=1,NC)
611   FORMAT(14X,D13.6,10X,D13.6)
608   FORMAT(5X,'PRESSURE TIMES DIFFUSIVITY:',4X,F9.6/)
      WRITE(6,613)PLEN,T
613   FORMAT(//17X,'PELLET LENGTH :',4X,F7.4/,15X,'TEMPERATURE (K) :',
     % 4X,F7.2/)
      WRITE(6,617)TCA
617   FORMAT(6X,'CRITICAL TEMPERATURE OF A:',4X,F7.3)
      WRITE(6,618)TCB
618   FORMAT(6X,'CRITICAL TEMPERATURE OF B:',4X,F7.3/)
      WRITE(6,619)PCA
619   FORMAT(9X,'CRITICAL PRESSURE OF A:',4X,F7.3)
      WRITE(6,618)PCB
620   FORMAT(9X,'CRITICAL PRESSURE OF B:',4X,F7.3/)
      WRITE(6,621)UA
621   FORMAT(9X,'AVG VISCOSITY OF A: ',4X,D10.3)
      WRITE(6,622)UB
622   FORMAT(9X,'AVG VISCOSITY OF B: ',4X,D10.3/)
C
C              READ IN THE VALUES OF THE CORRECTION FACTORS
C              AT THE INPUTTED VALUES OF PRESSURE FOR THE
C              DESIGNATED VALUE OF THE PARAMETER 'ALPHA'.
C              THESE VALUES WILL BE USED TO SUPPLY THE CORRECT
C              VALUE OF THE CORRECTION FACTORS AT THE DIFFERENT
C              PRESSURES ALONG THE LENGTH OF THE PELLET BY
C              LINEAR INTERPOLATION WITH THESE VECTORS.
C
      READ(5,*)NINT
      WRITE(6,*)NINT
```

```
      DO 1329 I=1,NINT
      READ(5,3131)ALP(I),P(I),CDF(I),CA(I),CB(I)
      WRITE(6,3131)ALP(I),P(I),CDF(I),CA(I),CB(I)
 3131 FORMAT(1X,D10.3,2X,D13.6,3X,F11.7,2X,F11.7,2X,F11.7)
 1329 CONTINUE
C
C           READ IN THE RATE CONSTANTS AND PELLET LENGTHS
C           TO BE ITERATED OVER.
C
      READ(5,*)NR
      DO 115 J=1,NR
      READ(5,*)XCONST(J)
  115 CONTINUE
      READ(5,*)NLEN
      DO 116 J=1,NLEN
      READ(5,*)XLENGTH(J)
  116 CONTINUE
C
C           RG1 AND RG2 ARE VALUES OF THE UNIVERSAL GAS CONSTANT
C           WITH UNITS OF ERG/(GMOL)(K) AND (ATM)(CM3)/(GMOL)(K),
C           RESPECTIVELY.
C
      RG1=8.317D07
      RG2=82.057
C
C          THE VALUES IN THE VECTOR PAR ARE VALUES WHICH ARE USED
C          MORE THAN ONCE IN THE PROGRAM AND ARE CALCULATED HERE
C          TO SIMPLIFY SUBSEQUENT CALCULATIONS.
C
      PAR(1)=C2*PDAB
      PAR(2)=C1*DSQRT(RG1*T/WMA)
      PAR(3)=C1*DSQRT(RG1*T/WMB)
      PAR(4)=RG2*T
      PAR(5)=DSQRT(WMA/WMB)
      PAR(6)=CO
C
C           CALCULATE THE ORTHOGONAL COLLOCATIONS DISCRETIZATION
C           MATRICES A AND B, USING THE SUBROUTINES JCOBI AND
C           DISCRT (DESCRIBED IN DETAIL IN "SOLUTION OF DIFFER-
C           ENTIAL EQUATION MODELS BY POLYNOMIAL APPROXIMATION",
C           BY VILLADSEN AND MICHELSEN, 1978).  AL AND BE DESIGNATE
C           THE TYPE OF POLYNOMIAL USED, ND INDICATES DIMENSION,
C           ID INDICATES THE CALCULATION OF ONLY THE MATRICES A
C           AND B, FOR FIRST AND SECOND ORDER DERIVATIVES, AND
```

```
C            NO=1 AND N1=1 INDICATES THAT BOUNDARY CONDITIONS
C            AT THE END POINTS ARE USED.
C
      AL=1.0
      BE=1.0
      ND= 50
      NO= 1
      N1= 1
      ID= 2
      CALL JCOBI(ND,NC,NO,N1,AL,BE,DIF1,DIF2,DIF3,DIF4,DIF5,ROOT)
      CALL DISCRT(ND,NC,NO,N1,ID,DIF1,DIF2,DIF3,DIF4,DIF5,ROOT,
     %  A,B,C,D)
C
      WRITE(6,53)(PAR(I),I=1,6)
  53  FORMAT(/25X,'THE VECTOR PAR',/,8(/24X,D14.7))
C
C           SET UP LOOPS TO SOLVE THE SYSTEM OF N SIMULTANEOUS
C           ALGEBRAIC EQUATIONS BY THE ROUTINE ZSYSTM AT THE
C           SPECIFIED VALUES OF THE RATE CONSTANTS AND VALUES
C           OF XO, THE GUESSED LENGTH AT WHICH YA=0.
C
      DO 1111 JI=1,NR
      RATEK=XCONST(JI)
      DO 9738 JX=1,NLEN
      XO=XLENGTH(JX)
      WRITE(6,1416)XO
 1416 FORMAT(/,15X,'THE VALUE OF XO  :',3X,F8.5)
      PAR(7)=PLEN*XO
C
      DO 1313 JL=1,N
      X(JL)=YX(JL)
 1313 CONTINUE
      ITMAX=CITMAX
C
      WRITE(6,1606)NORDER,RATEK                                         0000000
 1606 FORMAT(15X,'ORDER OF REACTION:',4X,I4/,15X,'RATE OF REACTION :', 0000000
     % 3X,D12.5/)                                                       0000000
C
C          CALL THE ROUTINE ZSYSTM TO SOLVE THE SET OF N
C          SIMULTANEOUS ALGEBRAIC EQUATIONS.  THE DIFFERENTIAL
C          EQUATIONS DESCRIBING THE MATERIAL BALANCE FOR THIS
C          CASE OF CHEMICAL REACTION IN A POROUS MATERIAL ARE
C          TRANSFORMED INTO ALGEBRAIC EQUATIONS USING THE
C          ORTHOGONAL COLLOCATION DISCRETIZATION MATRICES
```

```
C             PREVIOUSLY CALCULATED.  THE SET OF EQUATIONS ARE
C             DESCRIBED IN THE SUBROUTINE AUX, WITH THE SET OF
C             INDEPENDENT VARIABLES IN THE VECTOR X.  ZSYSTEM IS
C             AN IMSL, INC. ROUTINE AND IS FULLY DOCUMENTED IN
C             THE IMSL LIBRARY, EDITION 7, VERSION 8.1 (1979).
C             IER IS THE RETURN ERROR CODE WITH 'O' INDICATING
C             SOLUTION AT THE SPECIFIED ERROR CRITERIA WAS
C             ATTAINED.  THE SOLUTION PROCEDURE IN A NEWTON-LIKE
C             GAUSSIAN ELIMINATION WITH QUADRATIC CONVERGENCE.
C
C
      CALL ZSYSTM(AUX,EPS,NSIG,N,X,ITMAX,WA,PAR,IER)
      WRITE(6,51)ITMAX,IER
C
      DO 351 KI=1,NC2
      ZL(KI)=ROOT(KI)*PLEN*XO
 351  CONTINUE
  51  FORMAT(10X,'ITMAX ',I6,/,11X,'IER  ',I6,/)
C
C        OUTPUT CONCENTRATION AND PRESSURE PROFILE SOLUTIONS
C
      WRITE(6,52)
  52  FORMAT(/9X,'Z',14X,'W (ROOT)',11X,' YA ',12X,'  P  ',/)
      WRITE(6,1159)ZL(1),ROOT(1),YAO,PO
      DO 1158 K=1,NC
      KN=K+NC
      K1=K+1
      WRITE(6,1159)ZL(K1),ROOT(K1),X(K),X(KN)
 1159 FORMAT(3X,D13.6,5X,D13.6,4X,D13.6,4X,D13.6)
 1158 CONTINUE
      WRITE(6,1159)ZL(NC2),ROOT(NC2),BC3,BC4
C
 9738 CONTINUE
 1111 CONTINUE
C
C             IF THE CALCULATION OF THE EFFECTIVENESS FACTOR OR
C             MASS FLUXES IS NOT DESIRED, A VALUE OF 0 WAS
C             INPUTTED FOR IFEFF.  WITH A NON-ZERO VALUE,
C             CALCULATION OF THESE QUANTITIES WILL PROCEED.
C
       IF(IFEFF.EQ.0)GO TO 199
C
C             IF LAST PART OF THE CONCENTRATION PROFILE IS NOT
C             ENTIRELY MONOTONICALLY DECREASING, DUE TO NUMERICAL
```

```
C           SOLUTION ROUTINE, SMOOTH PROFILE BY LINEARLY
C           EXTRAPOLATING VALUES.  (DOING THIS HAS NEGLIGIBLE
C           EFFECT ON ANY RESULTS OF THE MASS FLUXES OR
C           EFFECTIVENESS FACTORS.
C
      NCM=NC-1
      DO 5887 MM=1,NCM
      IF(X(MM+1).GE.X(MM))X(MM+1)=X(MM)+(X(MM)-X(MM-1))*(ROOT(MM+2)
     % -ROOT(MM+1))/(ROOT(MM+1)-ROOT(MM))
 5887 CONTINUE
      BC3=X(NC)+(X(NC)-X(NCM))*(ROOT(NC2)-ROOT(NC2-1))/(ROOT(NC2-1)-
     % ROOT(NC2-2))
C
C           CALL THE SUBROUTINE EFF TO CALCULATE REACTION RATES
C           AND MASS FLUX VALUES ALONG THE PELLET LENGTH FOR
C           THE LAST COMPUTED VALUES OF THE RATE CONSTANT AND
C           XO WITH THE SOLUTION PROFILES.
C
      CALL EFF(X,XW,ROOT,PAR,RXNUM,DNA,DNB)
      WRITE(6,7152)
 7152 FORMAT(//5X,'(L*XO)**2*RX',10X,'NA',16X,'NB',10X,'FLUX RATIO'//)
      DO 1113 LK=1,NC2
      RATIO(LK)=DNB(LK)/DNA(LK)
C
C           IF REACTION RATES HAVE THE WRONG SIGN WHEN VERY
C           CLOSE TO ZERO DUE TO NUMBERICAL SOLUTION ERROR,
C           CHANGE TO PROPER SIGN.
C
      DO 5889 LL=1,NC2
      IF(RXNUM(LL).LE.0.0)RXNUM(LL)=-1.*RXNUM(LL)
 5889 CONTINUE
C
C               WRITE OUT RESULTS
C
      WRITE(6,7153)RXNUM(LK),DNA(LK),DNB(LK) ,RATIO(LK)
 7153 FORMAT(3X,D14.7,4X,D14.7,4X,D14.7,2X,D13.5)
 1113 CONTINUE
C
C           CALCULATE THE INTEGRAL PORTION IN THE DEFINITION
C           OF THE EFFECTIVENESS FACTOR WITH THE COMPUTED VECTOR
C           OR REACTION RATES.  WRITE OUT THE VALUE OF THE
C           INTEGRAL IF DESIRED.
C
      CALL  INTEGR(RXNUM,ROOT,SUMN,NC2)
```

```
C      WRITE(6,7125)SUMN
C7125  FORMAT(//,15X,'INTEGRAL OF RX',11X,D12.5)
C
C             CALCULATE THE VALUE OF THE EFFECTIVENESS FACTOR
C
       RXATO= YAO*PO/PAR(4)
       DEN= (PLEN**2)*XO*RATEK*(RXATO**NORDER)
       EFFAC= SUMN/DEN
       WRITE(6,7127)EFFAC
 7127  FORMAT(//15X,'EFFECTIVENESS FACTOR:',6X,F10.7)
C
 199   CONTINUE
C
       STOP
       END
C
C                      *****************
C                      *  SUBROUTINES  *
C                      *****************
C
C
C       THE FUNCTION SUBROUTINE AUX DEFINES THE SIMULTANEOUS
C       ALGEBRAIC EQUATIONS TO BE SOLVED BY THE ZSYSTM ROUTINE
C
       FUNCTION AUX(X,K,PAR)
       IMPLICIT REAL*8(A-H,O-Z)
       DIMENSION X(50),PAR(100)
       COMMON /Q2/ A(50,50),B(50,50),P(500),CDF(500),CA(500),CB(500)
       COMMON /Q3/ WMA,WMB,T,PO,XO,YAO,PDAB,PLEN,CO,C1,C2,RATEK,THETA
       COMMON /Q3A/ YN2,PN2,BC3,BC4,UA,UB
       COMMON /Q4/ NC,N,NORDER,NC2,NC1,NINT
C
C
C            IF K = 1,2,...N, (N IS THE NUMBER OF INTERNAL COLLOCATION
C            POINTS AND HALF THE NUMBER OF EQUATIONS TO BE SOLVED),
C            THEN USE EQUATION (1) FOR I=2,3,...N+1.  WHEN K=N+1,
C            N+2,...2N, USE EQ.(2) FOR I=2,3,...N+1.
C
C
       NN=NC+1
       NINT1=NINT-1
C
       IF(K.LE.NC)GO TO 1
       IF(K.GT.NC)GO TO 3
```

```
C
C                       DEFINE THE FIRST N EQUATIONS
C
    1 CONTINUE
      NK=NC+K
C
C           CALCULATE THE VALUES OF THE CORRECTION FACTORS
C           AT THE PRESSURE SPECIFIED IN THE VECTOR X BY
C           LINEAR INTERPOLATION OF THE TABULATED VALUES
C
      IF(X(NK).GE.P(1).AND.X(NK).LE.P(NINT))GO TO 551
      CD=1.0
      CSA=1.0
      CSB=1.0
      GO TO 553
C
  551 CONTINUE
      DO 554 L=1,NINT1
      LL=L+1
      IF(X(NK).LE.P(LL))CD=(X(NK)-P(L))/(P(LL)-P(L))
     % *(CDF(LL)-CDF(L)) + CDF(L)
      IF(X(NK).LE.P(LL))CSA=(X(NK)-P(L))/(P(LL)-P(L))
     % *(CA(LL)-CA(L)) + CA(L)
      IF(X(NK).LE.P(LL))CSB=(X(NK)-P(L))/(P(LL)-P(L))
     % *(CB(LL)-CB(L)) + CB(L)
      IF(X(NK).LE.P(LL))GO TO 553
C
  554 CONTINUE
  553 CONTINUE
C
C       CALCULATE THE VISCOSITY OF THE MIXTURE
C
      UM=(UA*X(K)*DSQRT(WMA)+UB*(1.-X(K))*DSQRT(WMB))/(X(K)*DSQRT(WMA)
     % +(1.0-X(K))*DSQRT(WMB))
C
C       CALCULATE THE COEFFICIENTS AT THE CURRENT VALUES OF YA AND P
C       OF THE SUMMATIONS IN THE FIRST SET OF N EQUATIONS
C
      ADEN=PAR(1)+(X(K)*(PAR(3)-PAR(2))+PAR(2))*X(NK)
      SA=CD*PAR(1)*PAR(2)*X(NK)/(ADEN*PAR(4))
      SB=(CSA*PAR(2)*(PAR(1)+PAR(3)*X(NK))/ADEN+PAR(6)*X(NK)*
     % 1.01325D06/UM)*X(K)/PAR(4)
      SBP=(CSB*PAR(3)*(PAR(1)+PAR(2)*X(NK))/ADEN+PAR(6)*X(NK)*
     % 1.01325D06/UM)*(1.-X(K))/PAR(4)
```

```
      CONE=-1.0*CD*PAR(1)*PAR(2)*(X(NK)**2)*(PAR(3)-PAR(2))/(PAR(4)
     % *ADEN*ADEN)
      CTWO=CD*(PAR(1)**2)*PAR(2)/(PAR(4)*ADEN*ADEN)
      CTHREE=CSA*PAR(2)*(PAR(1)+PAR(3)*X(NK))*(PAR(1)+PAR(2)*X(NK))
     % /(PAR(4)*ADEN*ADEN)+PAR(6)*X(NK)*1.01325D06/(UM*PAR(4))
C
      CFOUR=CSA*PAR(2)*PAR(3)*X(K)/(ADEN*PAR(4))-CSA*PAR(2)*X(K)
     % *(PAR(1)+PAR(3)*X(NK))*(X(K)*(PAR(3)-PAR(2))+PAR(2))/
     % (PAR(4)*ADEN*ADEN)+PAR(6)*X(K)*1.01325D06/(UM*PAR(4))
C
C        USING THE DISCRETIZATION MATRICES A AND B WITH THE
C        ORTHOGONAL COLLOCATION PROCEDURE, CALCULATE THE
C        VARIOUS SUMMATIONS IN THE EQUATIONS AT THE CURRENT
C        VALUE OF YA AND P
C
      V1=0.0
      V2=0.0
      V3=0.0
      V4=0.0
      V5=0.0
      V6=0.0
      I=K+1
C
C           V1= THE SUM OF B(I,J)Y(J) FOR J=2,3,....,N+1
C
      DO 10 J=2,NN
      V1=B(I,J)*X(J-1) +V1
   10 CONTINUE
C
C           V2= THE SUM OF A(N+2,J)Y(J) FOR J=2,3,....,N+1
C
      DO 11 J=2,NN
      V2=A(NC+2,J)*X(J-1) +V2
   11 CONTINUE
C
C           BC1=FIRST BOUNDARY CONDITION: MOLE FRAC AT W=0
C           BC2=SECOND B.C.:  PRESSURE AT W=0
C           BC3=THIRD B.C.: DY/DW=0 AT W=1
C
      BC1=YA0
      BC2=P0
      BC3=-(V2+A(NC+2,1)*BC1)/A(NC+2,NC+2)
C
C           V3= THE SUM OF A(I,J)Y(J) FOR J=2,3,....,N+1
```

```
C
      DO 12 J=2,NN
      V3=A(I,J)*X(J-1) +V3
   12 CONTINUE
C
C          V4= THE SUM OF A(I,J)P(J) FOR J=2,3,...,N+1
C
      DO 13 J=2,NN
      JJ=J-1+NC
      V4=A(I,J)*X(JJ) +V4
   13 CONTINUE
C
C          V5= THE SUM OF A(N+2,J)P(J) FOR J=2,3,...,N+1
C
      DO 14 J=2,NN
      JJ=J-1+NC
      V5=A(NC+2,J)*X(JJ)+V5
   14 CONTINUE
C
C          V6= THE SUM OF B(I,J)P(J) FOR J=2,3,...,N+1
C
      DO 15 J=2,NN
      JJ=J-1+NC
      V6=B(I,J)*X(JJ)+V6
   15 CONTINUE
C
C        BC4=FOURTH B.C.: DP/DW=0 AT W=1
C
      BC4= -(V5+A(NC+2,1)*BC2)/A(NC+2,NC+2)
C
C         DEFINE THE TERMS IN THE FIRST N EQUATIONS
C
      T1=(V1+B(I,1)*BC1+B(I,NC+2)*BC3)*SA
      T2=(V3+A(I,1)*BC1+A(I,NC+2)*BC3)
      T3=V4+A(I,1)*BC2+A(I,NC+2)*BC4
      T4=(V6+B(I,1)*BC2+B(I,NC+2)*BC4)*SB
      IF(NORDER.EQ.0)CRX=1.
      IF(NORDER.EQ.1)CRX=X(NK)*X(K)/PAR(4)
      IF(NORDER.EQ.2)CRX=(X(NK)*X(K)/PAR(4))*X(NK)*X(K)/PAR(4)
      T5=PAR(7)*PAR(7)*RATEK *CRX
C
C         DEFINE THE FIRST N EQUATIONS
C
      AUX=(T1+CONE*T2*T2+(CTWO+CTHREE)*T2*T3+CFOUR*T3*T3+T4-T5)
```

```
      RETURN
C
C
C          DEFINE THE SECOND N EQUATIONS
C
 3    CONTINUE
C
      KP=K
      KY=K-NC
      I=K-NC+1
C
C           DETERMINE THE CORRECTION FACTORS AS BEFORE
C
      IF(X(KP).GE.P(1).AND.X(KP).LE.P(NINT))GO TO 556
      CD=1.0
      CSA=1.0
      CSB=1.0
      GO TO 558
C
 556  CONTINUE
      DO 559 L=1,NINT1
      LL=L+1
      IF(X(KP).LE.P(LL))CD=(X(KP)-P(L))/(P(LL)-P(L))
     % *(CDF(LL)-CDF(L)) + CDF(L)
      IF(X(KP).LE.P(LL))CSA=(X(KP)-P(L))/(P(LL)-P(L))
     % *(CA(LL)-CA(L)) + CA(L)
      IF(X(KP).LE.P(LL))CSB=(X(KP)-P(L))/(P(LL)-P(L))
     % *(CB(LL)-CB(L)) + CB(L)
      IF(X(KP).LE.P(LL))GO TO 558
C
 559  CONTINUE
 558  CONTINUE
C
C            CALCULATE THE COEFFICIENTS OF THE SUMMATION
C            TERMS IN THE EQUATIONS, AS BEFORE
C
      UM=(UA*X(KY)*DSQRT(WMA)+UB*(1.-X(KY))*DSQRT(WMB))/(X(KY)
     % *DSQRT(WMA)+(1.0-X(KY))*DSQRT(WMB))
C
      ADEN=PAR(1)+(X(KY)*(PAR(3)-PAR(2))+PAR(2))*X(KP)
      SA=CD*PAR(1)*PAR(2)*X(KP)/(ADEN*PAR(4))
      SB=(CSA*PAR(2)*(PAR(1)+PAR(3)*X(KP))/ADEN+PAR(6)*X(KP)*
     % 1.01325D06/UM)*X(KY)/PAR(4)
      SBP=(CSB*PAR(3)*(PAR(1)+PAR(2)*X(KP))/ADEN+PAR(6)*X(KP)*
```

```
     % 1.01325D06/UM)*(1.-X(KY))/PAR(4)
      CONE=-1.0*CD*PAR(1)*PAR(2)*(X(KP)**2)*(PAR(3)-PAR(2))/(PAR(4)
     % *ADEN*ADEN)
      CTWO=CD*(PAR(1)**2)*PAR(2)/(PAR(4)*ADEN*ADEN)
C
      CFIVE=-1.0*CSB*PAR(3)*(PAR(1)+PAR(2)*X(KP))*(PAR(1)+PAR(3)*
     % X(KP))/(PAR(4)*ADEN*ADEN)-PAR(6)*X(KP)*1.01325D06/(UM*PAR(4))
C
      CSIX=CSB*PAR(3)*(1.0-X(KY))*(PAR(2)*ADEN-(PAR(1)+PAR(2)*X(KP))
     % *(X(KY)*(PAR(3)-PAR(2))+PAR(2)))/(PAR(4)*ADEN*ADEN)+
     % PAR(6)*(1.0-X(KY))*1.01325D06/(UM*PAR(4))
C
C             AGAIN CALCULATE THE SUMMATION VALUES AT THE CURRENT
C             VALUES OF YA AND P USING THE MATRICES A AND B.
C
      NN=NC+1
      V1=0.0
      V2=0.0
      V3=0.0
      V4=0.0
      V5=0.0
      V6=0.0
C
C           V1= THE SUM OF B(I,J)Y(J) FOR J=2,3,...,N+1
C
      DO 20 J=2,NN
      V1=B(I,J)*X(J-1)+V1
   20 CONTINUE
C
C           V2= THE SUM OF A(N+2,J)Y(J) FOR J=2,3,...,N+1
C
      DO 21 J=2,NN
      V2=A(NC+2,J)*X(J-1)+V2
   21 CONTINUE
C
C           BC1=FIRST BOUNDARY CONDITION: MOLE FRAC AT W=0
C           BC2=SECOND B.C.:  PRESSURE AT W=0
C           BC3=THIRD B.C.: DY/DW=0 AT W=1
C
      BC1=YA0
      BC2=P0
      BC3= -(V2+A(NC+2,1)*BC1)/A(NC+2,NC+2)
C
C           V3= THE SUM OF A(I,J)Y(J) FOR J=2,3,...,N+1
```

```
C
      DO 22 J=2,NN
      V3=A(I,J)*X(J-1)+V3
   22 CONTINUE
C
C            V4= THE SUM OF A(I,J)P(J) FOR J=2,3,...,N+1
C
      DO 23 J=2,NN
      JJ=J-1+NC
      V4=A(I,J)*X(JJ)+V4
   23 CONTINUE
C
C            V5= THE SUM OF A(N+2,J)P(J) FOR J=2,3,...,N+1
C
      DO 24 J=2,NN
      JJ=J-1+NC
      V5=A(NC+2,J)*X(JJ)+V5
   24 CONTINUE
C
C            V6= THE SUM OF B(I,J)P(J) FOR J=2,3,...,N+1
C
      DO 25 J=2,NN
      JJ=J-1+NC
      V6=B(I,J)*X(JJ)+V6
   25 CONTINUE
C
C          BC4=FOURTH B.C.: DP/DW=0 AT W=1
C
      BC4= -(V5+A(NC+2,1)*BC2)/A(NC+2,NC+2)
C
C
C
C           DEFINE THE TERMS IN THE SECOND N EQUATIONS
C
      T1=(V1+B(I,1)*BC1+B(I,NC+2)*BC3)*SA*PAR(5)
      T2=(V3+A(I,1)*BC1+A(I,NC+2)*BC3)
      T3=V4+A(I,1)*BC2+A(I,NC+2)*BC4
      T4=(V6+B(I,1)*BC2+B(I,NC+2)*BC4)*SBP
      IF(NORDER.EQ.0)CRX=1.
      IF(NORDER.EQ.1)CRX=X(KP)*X(KY)/PAR(4)
      IF(NORDER.EQ.2)CRX=(X(KP)*X(KY)/PAR(4))*(X(KP)*X(KY)/PAR(4))
      T5=PAR(7)*PAR(7)*THETA*RATEK * CRX
C
C           DEFINE THE SECOND N EQUATIONS
```

```
C
      AUX=(T1+PAR(5)*CONE*T2*T2+(PAR(5)*CTWO-CFIVE)*T2*T3-CSIX*T3*T3
     %  -T4-T5)
      RETURN
      END
C
C        THE SUBROUTINE PDIFF CALCULATES THE BINARY
C        DIFFUSIVITY TIMES THE PRESSURE USING THE ANALYTICAL
C        FORM GIVEN BY BIRD, STEWART, AND LIGHTFOOT, "TRANSPORT
C        PHENOMENA", 505 (1960).
C
      SUBROUTINE PDIFF(TCA,TCB,PCA,PCB,WMA,WMB,T,PDAB)
      IMPLICIT REAL*8(A-H,O-Z)
C
C
      A=0.0002745
      B=1.823
      C1=(PCA*PCB)**(1./3.)
      C2=(TCA*TCB)**(5./12.)
      C3=DSQRT((1./WMA) + (1./WMB))
      C4=T/((TCA*TCB)**0.5)
      PDAB=C1*C2*C3*A*(C4**B)
      RETURN
      END
C
C              SUBROUTINES JCOBI AND DISCRT CALCULATE THE ORTHOGONAL
C              COLLOCATION GRID POINTS AND THE DISCRETIZATION MATRICES
C              FOR THE ORDINARY DERIVATIVES.  THE SUBROUTINES
C              ARE DESCRIBED IN DETAIL IN "SOLUTION OF DIFFER-
C              ENTIAL EQUATION MODELS BY POLYNOMIAL APPROXIMATION",
C              BY VILLADSEN AND MICHELSEN, 1978).
C
      SUBROUTINE JCOBI(ND,N,NO,N1,AL,BE,DIF1,DIF2,DIF3,DIF4,DIF5,ROOT)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION DIF1(ND),DIF2(ND),DIF3(ND),DIF4(ND),DIF5(ND),ROOT(ND)
C
C         EVALUATION OF ROOTS AND DERIVATIVES OF JACOBI
C         POLYNOMIALS P(N) (AL,BE):  MACHINE ACCURACY 16 D.
C
C         FIRST EVALUATION OF COEFFICIENTS IN RECURSIVE
C         FORMULAS.  RECURSIVE COEFFICIENTS ARE STORED
C         IN DIF1 AND DIF2.
C
      AB=AL+BE
```

```
      AD=BE-AL
      AP=BE*AL
      DIF1(1)=(AD/(AB+2)+1)/2
      DIF2(1)=0.
      IF(N.LT.2)GO TO 15
      DO 10  I=2,N
      Z1=I-1
      Z=AB+2*Z1
      DIF1(I)=(AB*AD/Z/(Z+2)+1)/2
      IF(I.NE.2)GO TO 11
      DIF2(I)=(AB+AP+Z1)/Z/Z/(Z+1)
      GO TO 10
   11 Z=Z*Z
      Y=Z1*(AB+Z1)
      Y=Y*(AP+Y)
      DIF2(I)=Y/Z/(Z-1)
   10 CONTINUE
C
C            ROOT DETERMINATION BY NEWTON METHOD WITH
C            SUPRESSION OF PREVIOUSLY DETERMINED ROOTS
C
   15 X=0.
      DO 20  I=1,N
   25 XD=0.
      XN=1.
      XD1=0.
      XN1=0.
      DO 30  J=1,N
      XP=(DIF1(J)-X)*XN-DIF2(J)*XD
      XP1=(DIF1(J)-X)*XN1-DIF2(J)*XD1-XN
      XD=XN
      XD1=XN1
      XN=XP
   30 XN1=XP1
      ZC=1.
      Z=XN/XN1
      IF(I.EQ.1)GO TO 21
      DO 22  J=2,I
   22 ZC=ZC-Z/(X-ROOT(J-1))
   21 Z=Z/ZC
      X=X-Z
      IF(DABS(Z).GT.1.D-9)GO TO 25
      ROOT(I)=X
      X=X+.0001
```

```
   20 CONTINUE
C
C          ADD EVENTUAL INTERPOLATION POINTS AT X=0 OR
C          X=1
C
      NT=N+N0+N1
      IF(N0.EQ.0)GO TO 35
      DO 31 I=1,N
      J=N+1-I
   31 ROOT(J+1)=ROOT(J)
      ROOT(1)=0
   35 IF(N1.EQ.1)ROOT(NT)=1.
C
C          NOW EVALUATE DERIVATIVES OF POLYNOMIAL
C
      DO 40 I=1,NT
      X=ROOT(I)
      DIF1(I)=1.
      DIF2(I)=0.
      DIF3(I)=0.
      DIF4(I)=0.
      DIF5(I)=0.
      DO 40 J=1,NT
      IF(J.EQ.I)GO TO 40
      Y=X-ROOT(J)
      DIF5(I) = Y * DIF5(I) + 5. * DIF4(I)
      DIF4(I) = Y * DIF4(I) + 4. * DIF3(I)
      DIF3(I)=Y*DIF3(I)+3*DIF2(I)
      DIF2(I)=Y*DIF2(I)+2*DIF1(I)
      DIF1(I)=Y*DIF1(I)
   40 CONTINUE
      RETURN
      END
      SUBROUTINE DISCRT(ND,N,N0,N1,ID,DIF1,DIF2,DIF3,DIF4,DIF5,ROOT,
     1  A,B,C,D)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION DIF1(ND),ROOT(ND),DIF2(ND),DIF3(ND),DIF4(ND),DIF5(ND)
      DIMENSION A(ND,ND),B(ND,ND),C(ND,ND),D(ND,ND)
C
C         SUBROUTINE EVALUATES DISCRETIZATION MATRICES AND
C          GAUSSIAN QUADRATURE WEIGHTS NORMALIZED TO SUM OF ONE.
C          ID=1  DISCRETIZATION MATRIX FOR LI(1)(XJ) IN A(J,I)
C          ID=2  DISCRETIZATION MATRIX FOR LI(2)(XJ) IN B(J,I)
C                AND LI(1)(XJ) IN A(J,I)
```

```
C          ID=3  DISCRETIZATION MATRIX FOR LI(3)(XJ) IN C(J,I)
C                LI(2)(XJ) IN B(J,I), AND LI(1)(XJ) IN A(J,I).
C          ID=4  DISCRETIZATION MATRIX FOR LI(4)(XJ) IN D(J,I),
C                LI(3)(XJ) IN C(J,I), LI(2)(XJ) IN B(J,I), AND
C                LI(1)(XJ) IN A(J,I).
C
      NT=N+NO+N1
      DO 20 J=1,NT
      DO 20 I=1,NT
      Y=ROOT(J) - ROOT(I)
      IF(I.EQ.J) A(J,I) = DIF2(I)/DIF1(I)/2.
      IF(I.EQ.J) GO TO 20
      A(J,I) = DIF1(J)/DIF1(I)/Y
   20 CONTINUE
      IF(ID.EQ.1) RETURN
      DO 30 J=1,NT
      DO 30 I=1,NT
      Y=ROOT(J) - ROOT(I)
      IF(I.EQ.J) B(J,I) = DIF3(I)/DIF1(I)/3.
      IF(I.EQ.J) GO TO 30
      B(J,I) = 2.*(A(J,I)*A(J,J) - A(J,I)/Y)
   30 CONTINUE
      IF(ID.EQ.2) RETURN
      DO 40 J=1,NT
      DO 40 I=1,NT
      Y=ROOT(J) - ROOT(I)
      IF(I.EQ.J) C(J,I)= DIF4(I)/DIF1(I)/4.
      IF(I.EQ.J) GO TO 40
      C(J,I) = 3.*(A(J,I)*B(J,J) - B(J,I)/Y)
   40 CONTINUE
      IF(ID.EQ.3) RETURN
      DO 50 J=1,NT
      DO 50 I=1,NT
      Y=ROOT(J) - ROOT(I)
      IF(I.EQ.J) D(J,I) = DIF5(I)/DIF1(I)/5.
      IF(I.EQ.J) GO TO 50
      D(J,I) = 4.*(A(J,I)*C(J,J) - C(J,I)/Y)
   50 CONTINUE
      RETURN
      END
C
C
C               SUBROUTINE EFF SUBSTITUTES THE SOLUTION VECTOR OF
C               THE CONCENTRATION AND PRESSURE PROFILES ALONG THE
```

```
C             PELLET LENGTH AS DETERMINED BY THE IMSL ROUTINE
C             ZSYSTM INTO THE SET OF ALGEBRAIC EQUATIONS TO GIVE
C             THE REACTION RATES AND MASS FLUXES ALONG THE
C             PELLET LENGTH.  THE EQUATIONS ARE ABOUT THE SAME AS
C             DESCRIBED IN THE SUBROUTINE AUX BUT ARE NOW ONLY
C             EVALUATED AT THE CORRECTED SOLUTION VECTOR.
C
      SUBROUTINE EFF(X,XW,ROOT,PAR,RXNUM,DNA,DNB)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(50),PAR(100),ROOT(50),RXNUM(50)
      DIMENSION XW(50),DNA(50),DNB(50)
      COMMON /Q2/ A(50,50),B(50,50),P(500),CDF(500),CA(500),CB(500)
      COMMON /Q3/ WMA,WMB,T,PO,XO,YAO,PDAB,PLEN,CO,C1,C2,RATEK,THETA
      COMMON /Q3A/ YN2,PN2,BC3,BC4,UA,UB
      COMMON /Q4/ NC,N,NORDER,NC2,NC1,NINT
C
C

      NN=NC+1
      NINT1=NINT-1
C
      NC3=NC+3
      N4=2*NC2
C
C             DEFINE THE BOUNDARY VALUES
C
      XW(1)=YAO
      XW(NC2)=BC3
      XW(NC2+1)=PO
      XW(N4)=BC4
      DO 80 IB=1,NC
      XW(IB+1)=X(IB)
      XW(IB+NC3)=X(IB+NC)
   80 CONTINUE
C
      DO 101 I=1,NC2
      K=I
      NK=K+NC2
C
C             CALCULATE THE CORRECTION FACTORS
C
      IF(XW(NK).GE.P(1).AND.XW(NK).LE.P(NINT))GO TO 551
      CD=1.0
      CSA=1.0
      CSB=1.0
```

```
      GO TO 553
C
 551  CONTINUE
      DO 554 L=1,NINT1
      LL=L+1
      IF(XW(NK).LE.P(LL))CD=(XW(NK)-P(L))/(P(LL)-P(L))
    %  *(CDF(LL)-CDF(L)) + CDF(L)
      IF(XW(NK).LE.P(LL))CSA=(XW(NK)-P(L))/(P(LL)-P(L))
    %  *(CA(LL)-CA(L)) + CA(L)
      IF(XW(NK).LE.P(LL))CSB=(XW(NK)-P(L))/(P(LL)-P(L))
    %  *(CB(LL)-CB(L)) + CB(L)
      IF(XW(NK).LE.P(LL))GO TO 553
C
 554  CONTINUE
 553  CONTINUE
C
C           CALCULATE THE TERMS IN THE ALGEBRAIC EQUATIONS
C           AT THE VALUES IN THE SOLUTION VECTOR XW
C
      UM=(UA*XW(K)*DSQRT(WMA)+UB*(1.-XW(K))*DSQRT(WMB))/(XW(K)*
    %  DSQRT(WMA)+(1.0-XW(K))*DSQRT(WMB))
      ADEN=PAR(1)+(XW(K)*(PAR(3)-PAR(2))+PAR(2))*XW(NK)
      SA=CD*PAR(1)*PAR(2)*XW(NK)/(ADEN*PAR(4))
      SB=(CSA*PAR(2)*(PAR(1)+PAR(3)*XW(NK))/ADEN+PAR(6)*XW(NK)*
    %  1.01325D06/UM)*XW(K)/PAR(4)
      SBP=(CSB*PAR(3)*(PAR(1)+PAR(2)*XW(NK))/ADEN+PAR(6)*XW(NK)*
    %  1.01325D06/UM)*(1.-XW(K))/PAR(4)
      CONE=-1.0*CD*PAR(1)*PAR(2)*(XW(NK)**2)*(PAR(3)-PAR(2))/(PAR(4)
    %  *ADEN*ADEN)
      CTWO=CD*(PAR(1)**2)*PAR(2)/(PAR(4)*ADEN*ADEN)
      CTHREE=CSA*PAR(2)*(PAR(1)+PAR(3)*XW(NK))*(PAR(1)+PAR(2)*XW(NK))
    %  /(PAR(4)*ADEN*ADEN)+PAR(6)*XW(NK)*1.01325D06/(UM*PAR(4))
C
      CFOUR=CSA*PAR(2)*PAR(3)*XW(K)/(ADEN*PAR(4))-CSA*PAR(2)*XW(K)
    %  *(PAR(1)+PAR(3)*XW(NK))*(XW(K)*(PAR(3)-PAR(2))+PAR(2))/
    %  (PAR(4)*ADEN*ADEN)+PAR(6)*XW(K)*1.01325D06/(UM*PAR(4))
C
      V1=0.0
      V2=0.0
      V3=0.0
      V4=0.0
      V5=0.0
      V6=0.0
C
```

```
C           V1= THE SUM OF B(I,J)Y(J) FOR J=1,2,...,NC2
C
      DO 10 J=1,NC2
      V1=B(I,J)*XW(J) +V1
   10 CONTINUE
C
C
C           V3= THE SUM OF A(I,J)Y(J) FOR J=1,2,...,NC2
C
      DO 12 J=1,NC2
      V3=A(I,J)*XW(J) +V3
   12 CONTINUE
C
C           V4= THE SUM OF A(I,J)P(J) FOR J=1,2,...,NC2
C
      DO 13 J=1,NC2
      JJ=J+NC2
      V4=A(I,J)*XW(JJ) +V4
   13 CONTINUE
C
C           V6= THE SUM OF B(I,J)P(J) FOR J=1,2,...,NC2
C
      DO 15 J=1,NC2
      JJ=J+NC2
      V6=B(I,J)*XW(JJ)+V6
   15 CONTINUE
C
C
C
C
      T1= V1*SA
      T2= V3
      T3= V4
      T4= V6*SB
C
C           DEFINE RXNUM(I), DNA(I), AND DNB(I) AT THE ITH POINT
C
      DNA(I)=(-SA*V3-SB*V4)/PAR(7)
      DNB(I)=(SA*PAR(5)*V3 - SBP*V4)/PAR(7)
      RXNUM(I)=(T1+CONE*T2*T2+(CTWO+CTHREE)*T2*T3+CFOUR*T3*T3+T4 )
  101 CONTINUE
      RETURN
      END
C
```

```
C
C           SUBROUTINE INTEGR CALCULATES THE INTEGRAL PORTION
C           (NUMERATOR) IN THE EFFECTIVENESS FACTOR DEFINITION
C           USING THE CALCULATED VALUES OF THE REACTION RATES.
C           SIMPSON'S RULE FOR UNEVENLY SPACE POINTS IS USED
C
       SUBROUTINE INTEGR(RXNUM,ROOT,SUMN,NC2)
       IMPLICIT REAL*8(A-H,O-Z)
       DIMENSION XW(50),RXNUM(50),ROOT(50)
C
C             CALCULATE THE INTEGRAL PORTION OF THE EFFECTIVENESS
C             FACTOR BY SUMMING THE REACTION RATES ALONG THE
C             PELLET LENGTH USING SIMPON'S RULE FOR UNEVENLY
C             SPACE BASED POINTS, WHICH ARE SPECIFIED BY ROOT.
C             ONLY AN ODD NUMBER OF BASE POINTS ARE USED HERE.
C             SINCE THE REACTION RATES ALONG THE PELLET LENGTH
C             MAY BE CLOSE TO ZERO AFTER A CERTAIN LENGTH AS
C             YA GOES TO ZERO, AND MAY FLUCTUATE POSITIVELY AND
C             NEGATIVELY AROUND ZERO, YOU MAY CHOOSE TO USE ONLY
C             A CERTAIN NUMBER OF POINTS ALONG THE PELLET TO
C             INTEGRATE WITH.  NC2 IS THE NUMBER OF POINTS ALONG
C             THE PELLET AT WHICH THE REACTION RATES ARE CALCULATED.
C             THIS MAY BE SET SMALLER IF DESIRED SO AS TO NOT
C             INCLUDE FLUCUATING REACTION RATES.  THE ERROR IS
C             GENERALLY NOT VERY LARGE IN EITHER CASE.
C
C       NC2= 8
C
        ITERP= (NC2-1)*0.5
        ATERP= (NC2-1)*0.5
        IT2= ATERP +0.6
        IF(IT2.GT.ITERP)ROOT(NC2+1)=ROOT(NC2-1)
        IF(IT2.GT.ITERP)ROOT(NC2-1)=ROOT(NC2)
        IF(IT2.GT.ITERP)RXNUM(NC2+1)=RXNUM(NC2-1)
        IF(IT2.GT.ITERP)RXNUM(NC2-1)=RXNUM(NC2)
        SUMN=0.0
 C
        DO 10 K=1,ITERP
        I=2*K-1
        WI1=ROOT(I)
        WI2=ROOT(I+1)
        WI3=ROOT(I+2)
        R1=RXNUM(I)
        R2=RXNUM(I+1)
```

```
      R3=RXNUM(I+2)
      DD21=(R2-R1)/(WI2-WI1)
      DD32=(R3-R2)/(WI3-WI2)
      DD321=(DD32-DD21)/(WI3-WI1)
      SUM= R1*(WI3-WI1) + ((WI3*WI3-WI1*WI1)*0.5- WI1*(WI3-WI1))
     $ *DD21 + ((WI3*WI3*WI3-WI1*WI1*WI1)/3 - (WI1+WI2)*(WI3*WI3
     $ -WI1*WI1)*0.5 + WI1*WI2*(WI3-WI1))*DD321
      SUMN=SUMN+SUM
 10   CONTINUE
C
      IF(IT2.GT.ITERP)ROOT(NC2-1)=ROOT(NC2+1)
      IF(IT2.GT.ITERP)RXNUM(NC2-1)=RXNUM(NC2+1)
C
      RETURN
      END
```

```
              **********************
              * SAMPLE INPUT DATA *
              **********************

  1.D-08,4,25
   12
0.8611,0.6232,0.3975,0.2337,0.1310,0.0721,
0.0391,0.0223,0.0139,0.0100,0.0090,0.0080
1.0005,1.0015,1.0022,1.0031,1.0036,1.0041,
1.0044,1.0046,1.0046,1.00467,1.00468,1.00468
         1,1
  32.0
  16.0
  299.26
  1.0
  1.0
  1.0
 500.D-12,0.100D-04,0.50
  310.0,190.0,50.0,60.0,120.D-06,140.D-06
 12
 0.100D-03    0.995000D+00      0.8717073     1.0001053     0.9998514
 0.100D-03    0.100000D+01      0.8720452     1.0001045     0.9998525
 0.100D-03    0.100100D+01      0.8721126     1.0001043     0.9998527
 0.100D-03    0.100200D+01      0.8721798     1.0001042     0.9998530
 0.100D-03    0.100300D+01      0.8722469     1.0001040     0.9998532
 0.100D-03    0.100400D+01      0.8723140     1.0001039     0.9998534
 0.100D-03    0.100500D+01      0.8723810     1.0001037     0.9998536
 0.100D-03    0.100600D+01      0.8724478     1.0001036     0.9998539
 0.100D-03    0.100700D+01      0.8725146     1.0001034     0.9998541
 0.100D-03    0.100800D+01      0.8725813     1.0001032     0.9998543
 0.100D-03    0.100900D+01      0.8726479     1.0001031     0.9998545
 0.100D-03    0.101900D+01      0.8727145     1.0001029     0.9998547
   1
 2.097D+00
   1
   0.8407
```

```
          *************************
          * SAMPLE OUTPUT RESULTS *
          *************************

          ORDER OF REACTION:         1

      MOLECULAR WEIGHT OF A       32.000
      MOLECULAR WEIGHT OF B       16.000

    THETA=MOL WT A/MOL WT B:      2.0000

         THE GEOMETRIC PARAMETERS OF THE PELLET

               C0            C1             C2

          0.500D-09     0.100D-04     0.500D+00

 PRESSURE TIMES DIFFUSIVITY:      0.172581

                      INITIAL PROFILE

                YA                       P

          0.861100D+00            0.100050D+01
          0.623200D+00            0.100150D+01
          0.397500D+00            0.100220D+01
          0.233700D+00            0.100310D+01
          0.131000D+00            0.100360D+01
          0.721000D-01            0.100410D+01
          0.391000D-01            0.100440D+01
          0.223000D-01            0.100460D+01
          0.139000D-01            0.100460D+01
          0.100000D-01            0.100467D+01
          0.900000D-02            0.100468D+01
          0.800000D-02            0.100468D+01

            PELLET LENGTH :        1.0000
          TEMPERATURE (K) :        299.26

   CRITICAL TEMPERATURE OF A:     310.000
   CRITICAL TEMPERATURE OF B:     190.000
```

```
        CRITICAL PRESSURE OF A:      50.000
     CRITICAL TEMPERATURE OF B:      60.000

        AVG VISCOSITY OF A:       0.120D-03
        AVG VISCOSITY OF B:       0.140D-03

         12
0.100D-03     0.995000D+00       0.8717073      1.0001053      0.9998514
0.100D-03     0.100000D+01       0.8720452      1.0001045      0.9998525
0.100D-03     0.100100D+01       0.8721126      1.0001043      0.9998527
0.100D-03     0.100200D+01       0.8721798      1.0001042      0.9998530
0.100D-03     0.100300D+01       0.8722469      1.0001040      0.9998532
0.100D-03     0.100400D+01       0.8723140      1.0001039      0.9998534
0.100D-03     0.100500D+01       0.8723810      1.0001037      0.9998536
0.100D-03     0.100600D+01       0.8724478      1.0001036      0.9998539
0.100D-03     0.100700D+01       0.8725146      1.0001034      0.9998541
0.100D-03     0.100800D+01       0.8725813      1.0001032      0.9998543
0.100D-03     0.100900D+01       0.8726479      1.0001031      0.9998545
0.100D-03     0.101900D+01       0.8727145      1.0001029      0.9998547
                         THE VECTOR PAR

                         0.8629050D-01
                         0.2788898D+00
                         0.3944098D+00
                         0.2455638D+05
                         0.1414214D+01
                         0.5000000D-09


               THE VALUE OF XO  :     0.84070
               ORDER OF REACTION:       1
               RATE OF REACTION :     0.20970D+01

          ITMAX      15
           IER        0

        Z                W (ROOT)             YA                 P

  0.000000D+00       0.000000D+00       0.100000D+01       0.100000D+01
  0.168413D-01       0.200325D-01       0.860935D+00       0.100045D+01
  0.555698D-01       0.660995D-01       0.622783D+00       0.100134D+01
  0.113970D+00       0.135566D+00       0.397558D+00       0.100239D+01
```

```
0.188889D+00        0.224680D+00        0.233734D+00        0.100333D+01
0.276286D+00        0.328638D+00        0.130624D+00        0.100401D+01
0.371450D+00        0.441834D+00        0.712304D-01        0.100445D+01
0.469250D+00        0.558166D+00        0.389881D-01        0.100470D+01
0.564414D+00        0.671362D+00        0.222232D-01        0.100484D+01
0.651811D+00        0.775320D+00        0.138699D-01        0.100490D+01
0.726730D+00        0.864434D+00        0.999995D-02        0.100494D+01
0.785130D+00        0.933901D+00        0.847779D-02        0.100495D+01
0.823859D+00        0.979968D+00        0.806958D-02        0.100495D+01
0.840700D+00        0.100000D+01        0.803247D-02        0.100495D+01

 (L*XO)**2*RX            NA                  NB              FLUX RATIO

0.5996802D-04       0.1109840D-04       -0.2282575D-04      -0.20567D+01
0.5198601D-04       0.9838350D-05       -0.2015563D-04      -0.20487D+01
0.3763824D-04       0.7500005D-05       -0.1526439D-04      -0.20353D+01
0.2405269D-04       0.5054162D-05       -0.1022068D-04      -0.20222D+01
0.1415373D-04       0.3098792D-05       -0.6238036D-05      -0.20131D+01
0.7915927D-05       0.1779727D-05       -0.3572282D-05      -0.20072D+01
0.4317746D-05       0.9824152D-06       -0.1968987D-05      -0.20042D+01
0.2364947D-05       0.5346318D-06       -0.1070668D-05      -0.20026D+01
0.1346376D-05       0.2917867D-06       -0.5842251D-06      -0.20022D+01
0.8442972D-06       0.1593381D-06       -0.3192698D-06      -0.20037D+01
0.5970841D-06       0.8468703D-07       -0.1694601D-06      -0.20010D+01
0.5603676D-06       0.3672241D-07       -0.7476534D-07      -0.20360D+01
0.1739923D-06       0.1856585D-07       -0.3306597D-07      -0.17810D+01
0.1409306D-05       0.3553192D-07       -0.5024972D-07      -0.14142D+01

          EFFECTIVENESS FACTOR:         0.1330283
```

APPENDIX D

CONCLUSIONS

The modified dusty-gas model accounts for the effects that the pore-size and tortuosity distributions have on the mass fluxes of species in porous media, particularly in the transition transport regime. The behavior of the modified dusty-gas model is similar to that obtained from the dusty-gas equations when the system pressure is either very low or very high, as well as for intermediate pressures when the characteristic parameter of the effectiveness function, $\Delta(R)$, has a very small value. At either pressure extreme, essentially all pores in a porous medium are in a single transport regime, either Knudsen or molecular. At intermediate operation pressures, for a porous medium with a wide pore-size distribution, the relative mass flux contribution will vary with the pore radii since the transport mechanisms vary. But as the value of the parameter α in the function $\Delta(R)$ becomes very small, then $\Delta(R)$ places uniform emphasis on all pore radii for a given pressure, and thus, both models have similar behavior.

The effectiveness function $\Delta(R)$ is inversely related to the tortuosity distribution and is a weighting function for the volume pore-size distribution $V(R)$. The modified dusty-gas model takes both the tortuosity and the pore-size distributions of the porous medium into account, while the dusty-gas model averages experimental data to represent a heteroporous system as a hypothetical homoporous system. The transport behavior of a homoporous system is very much like that in a cylindrical pore of constant diameter. A cylindrical pore has its entire volume available for axial transport along the pellet length but the available volume for axial transport is smaller for an actual pore due to its tortuous path. The function $\Delta(R)$ indicates the fraction of volume available for transport at the different pore radii. The product $\Delta(R)V(R)$ provides the effective volume for transport and the parameter α in $\Delta(R)$ defines a shape for the effectiveness function that indicates the relative importance of the various pore radii to the total transport flux.

A comparison of the fluxes predicted by the modified dusty-gas (heteroporous model) and the dusty-gas (homoporous model) models for the physical systems examined in this work shows that the dusty-gas model always predicts larger fluxes than those estimated by the modified dusty-gas model, since the effective volume for transport is generally less for a heteroporous medium when compared to a homoporous system. The results presented indicate that the dusty-gas model could fail in predicting accurately the mass transport behavior of gases in porous media with wide pore-size distributions. For the examined cases of binary isobaric diffusion, simultaneous diffusion and flow, and chemical reactions with mole changes, values of the parameter α were considered that showed significant deviations in the predictions of the mass fluxes and effectiveness factors by the modified dusty-gas model relative to the predictions of the dusty-gas model; over 74% for simultaneous diffusion and flow, over 66% for the case of binary isobaric diffusion, and over 30% for the case of chemical reactions with mole changes. However, it should be noted that, although a range of values for α was considered for the two pore-size distributions used, the value of α that is characteristic for each pore-size distribution is not known because comparisons with experimental data were not made since such data were not available. The value of the parameter α, like the values of C_0, C_1, and C_2, should be determined from experimental data for each porous medium. A range of values of α was considered solely for purposes of comparing the behavior of the modified dusty-gas and the dusty-gas models.

The results have also shown that varying the parameters C_0, C_1, or C_2 can cause a significant change in the magnitudes of the mass fluxes for both components in the binary system. However, the results show that, in general, the percentage change in the fluxes predicted by the modified dusty-gas model with respect to the fluxes predicted by the dusty-gas model is approximately the same throughout the range of values of the parameters.

Since many adsorbents, membranes, and catalysts are heterporous and operate in the transition region of transport, it is suggested that the modified dusty-gas model should be used to describe mass transfer in the design equations of industrial separation and chemical reaction systems.

APPENDIX E

RECOMMENDATIONS

Possibilities for futher work arising out of the material of this thesis are discussed below:

(1) The equations of the modified dusty-gas model were solved for the geometry of a one-dimensional slab. The equations should also be solved for cylindrical and spherical systems.

(2) The parameters C_0, C_1, C_2 and α in the modified dusty-gas model should be estimated from experimental data obtained from steady-state permeability and binary isobaric diffusion experiments, and fitted to the equations of the modified dusty-gas model for selected porous media with various pore-size distributions. With these values, the predictions of the modified dusty-gas and the dusty-gas models should be compared with experimental results for various sets of operating conditions in the porous media considered in the experimental study.

(3) An exponential expression was postulated for the effectiveness function $\Delta(R)$ which qualitatively satisfies the expected form. Other expressions for $\Delta(R)$ are also possible which are qualitatively correct and could be tested to determine the sensitivity of the correction factors to the form of $\Delta(R)$. One possible expression that might be examined is

$$\Delta(R) = \frac{\alpha R}{1 + \alpha R} \qquad \text{(E-1)}$$

(4) The model and solution approach for irreversible chemical reactions with mole changes should be extended to other types of reactions and reaction networks, and comparisons should be made between the effectiveness factors estimated by the modified dusty-gas and the dusty-gas models. Also, chemical reaction experiments with different porous catalysts should be carried out, and the predictions of the two models should be compared with the experimental data.

(5) The effects of temperature could be added to the modified dusty-gas model to take into account thermal transpiration, thermal diffusion, and especially the thermal effects associated with the heat of reaction when a chemical reaction occurs in a porous medium.

(6) An attempt should be made to extend the modified dusty-gas equations presented for a binary system to a system containing three or more components. Since the equations would be implicit in the mass fluxes, the solution procedure would be difficult for a number of components greater than two. The effect of the additional components on the constitutive forms of the diffusivities would also have to be considered.

(7) An attempt may also be made to determine a theoretical estimate for α based, perhaps, on the pore-size distribution and the geometric information provided by the parameters C_1 and C_2. The Minimum Energy Principle may prove helpful in providing a framework for a theoretical estimation of α.

APPENDIX F

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