i = species, $i = 1, \ldots, (n-1), I$
m = mass transfer
0 = initial
s = in the gas phase, just adjacent to the interface
t = in the transferred state, for example, $m_{i,t} = n_{i,s}/\dot{m}''$
u = in the liquid phase, just adjacent to the interface

Superscripts

$*$ = limit of zero net mass transfer ($\dot{m}'' \to 0$)
l = liquid phase

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Comments on the Note by Mills

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The authors wish to thank Professor Mills (1973) for his note pointing to the relation between our droplet model (Newbold and Amundson, 1973) and the earlier models of Spalding (1963) and Bird et al. (1960).

The exact relation between the mass transfer models can be found by substituting for $B_{m,i}$, $g^*_{m,i}$ and $m_{i,t} = n_{i,s}/\dot{m}''$ in Mills' equation (1) to get

$$\dot{m}'' = \frac{\rho D_{im}}{r} \ln\left[1 + \frac{m_{i,e} - m_{i,s}}{m_{i,s} - n_{i,s}/\dot{m}''}\right] \tag{1}$$

and then solving for $n_{i,s}$ to arrive at the expression

$$n_{i,s} = \dot{m}'' \left\{ \frac{m_{i,s} \exp\left(\dfrac{\dot{m}'' r}{\rho D_{im}}\right) - m_{i,e}}{\exp\left(\dfrac{\dot{m}'' r}{\rho D_{im}}\right) - 1} \right\} \tag{2}$$

Equation (2) is readily seen to be the mass basis equivalent of our Equation (28) [not Equation (35) as Mills suggests]:

$$J_i = \overline{J} \left[\frac{y_i^* \exp\left(\dfrac{\overline{J} r}{C_T D_{im}}\right) - y_{iB}}{\exp\left(\dfrac{\overline{J} r}{C_T D_{im}}\right) - 1} \right] \tag{3}$$

Our development continues from this point to eliminate the total flux $\overline{J}$ (by assuming the flux of inert J_I equals zero), and arrives finally at an explicit expression [Equation (35) in our paper] for the flux of component i:

$$J_i = \frac{1}{r} \frac{C_T D_{Im}}{P_T} \ln(C) \left[\frac{x_i P_{Ai}^* C^{D_{Im}/D_{im}} - P_{Ai}}{C^{D_{Im}/D_{im}} - 1} \right] \tag{4}$$

where

$$C = \frac{P_T - \sum_{i=1}^{n} P_{Ai}}{P_T - \sum_{i=1}^{n} x_i P_{Ai}^*} \tag{5}$$

The advantages of this explicit formulation over Mills' implicit Equation (1) become evident when one attempts to deduce the properties of the model. For example, in order to prove, via the earlier formulation, that the boiling point cannot be exceeded, Mills finds it necessary to argue that $T \to T_{B.P.}$ implies $m_{i,s} \to m_{i,t} = n_{i,s}/\dot{m}''$. However intuitive it might seem that $m_{i,s} \to n_{i,s}/\dot{m}''$, this behavior isn't necessarily related to the model in question. (In fact, if we were willing to make an assumption of this kind we might just as well assume that the boiling point will not be exceeded.) In comparison, the boiling point property can be deduced directly from our Equations (4) and (5) above, since, by definition, the denominator of C vanishes at the boiling point.

As to Mills' assertion that the earlier formulation is advantageous because it can be applied to evaporation in flowing, as well as stagnant gases, we maintain that our formulation can be extended to this case as well. For example, if the mass transfer problem posed in our article is solved for a finite (rather than infinite) stagnant film we get

$$J_i = \frac{N_{Sh}}{2} \frac{1}{r} \frac{C_T D_{Im}}{P_T} \ln(C) \left[\frac{x_i P_{Ai}^* C^{D_{Im}/D_{im}} - P_{Ai}}{C^{D_{Im}/D_{im}} - 1} \right] \tag{6}$$

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where the Sherwood number N_{Sh} can be related to the flowing stream by any one of a number of standard correlations. In addition, our formulae can be extended to include radiation and intraparticle transport with the same ease as Spalding's formulae.

In summary, it has been shown that (1) Spalding's model is equivalent to ours at an intermediate state, (2) our final formulation is more amenable to analysis than Spalding's and (3) the advantages which Mills attributes to Spalding's formulation are realized by our formulation as well.

NOTATION

See Newbold and Amundson (1973) as well as Mills' notation.

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A Model for the Application of Gas Chromatography to Measurements of Diffusion in Bidisperse Structured Catalysts

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In a recent article, Ma and Mancel (1972) reported the results of their investigation of the diffusion of gases in zeolites by the gas chromatography (GC) technique. They discuss the fact that the effective diffusivity derived from their results is due to some combination of contributions from macropore and micropore diffusion terms. The precise manner in which these two diffusion terms combine, however, is not known. This is because the theory of transient behavior of chromatograph columns developed originally by van Deemter et al. (1956) and extended and improved by Suzuki and Smith (1971) is applicable only to catalysts possessing a unimodal pore size distribution.

This note describes a model of transient diffusion in a GC column which we believe to be applicable to bidisperse structured catalyst particles, that is, particles characterized by two peaks in the distribution of pore sizes. The model does not require that the peaks be sharply defined. A bidisperse structured catalyst may be formed by compressing, extruding, or in some other manner compacting finely powdered microporous material into a pellet. Ideally the micropores are due to porosity inherent in the individual microparticles of catalyst. The macropores result from voids between the microparticles after pelletization or extrusion.

THE MODEL

A single effective diffusion coefficient cannot adequately characterize the mass transfer within a bidisperse structured catalyst when the contributions from both pore systems are substantial. In a realistic model the separate identity of the macropore and micropore structures must be maintained, and the diffusion must be described in terms of two coefficients, an effective macropore diffusivity, and an effective micropore diffusivity. Mingle and Smith (1961) and Carberry (1962) employed such a macro-micro-pore model in their evaluation of effectiveness factors in bidisperse structured catalysts. More recently Rukenstein et al. (1971) used the macro-micro-pore model in their study of sorption rates of gases and vapors in ion exchange resins. The model as applied to the GC effective diffusivity experiment is illustrated in Figure 1. This model might be expected to apply when the diffusivity in the micropores or microparticles D_x is considerably smaller than the macropore diffusivity D_y for only in this circumstance can the microparticle contribution to the radial flux in the catalyst particle be neglected. In our development we have employed a moments analysis to this model of pore structure to obtain an equation relating quantities extracted from the chromatogram to the model parameters.

A mass balance on the diffusing species across a differential element of microparticle results in the following partial differential equation with boundary conditions:

$$\frac{\partial^2 C_x}{\partial x^2} + \frac{2}{x}\,\frac{\partial C_x}{\partial x} = \frac{\theta_x}{D_x}\,(1 + K_a)\,\frac{\partial C_x}{\partial t} \qquad (1)$$

$$C_x(R_x, t) = C_y(y, t) \qquad (2)$$