
A SIMPLIFIED DESCRIPTION OF MULTICOMPONENT DIFFUSION IN POROUS MEDIA. II. CONDITIONS FOR NEGLIGIBLE FORCED FLOW EFFECTS

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Conditions are examined permitting the pressure gradient appearing in a porous catalyst sustaining multicomponent diffusion of a gas mixture accompanied by chemical reaction to be neglected. Deviations are computed of the sum of mole fractions from unity for selected typical cases as a measure of error committed by neglecting the forced flow.

With the exception of the simplest systems the majority of reactions of industrial importance leads to several products. Maximum selectivity or maximum yield of the desired product in these cases have usually the highest priority overriding criteria for maximum conversion of reactants.

An important step in the study of mass transport in porous catalysts as affecting selectivity of a system of heterogeneous catalytic reactions is adequate description of the flow of multicomponent reaction mixture incorporating flow terms into the differential mass balances of reacting species. The problem of a thorough description of the flow of multicomponent mixture in a system undergoing several chemical reactions has not been systematically studied. Description of mass transport is usually reduced to the case of the diffusional flux of the reaction mixture with the diffusion being either of purely Knudsen or molecular type with mutually independent and constant (independent of the concentration of the species) appropriate effective diffusion coefficients of the species. The diffusion of individual species is then described by the Fick law in the form for a binary mixture. These simplifications, of course, are at odds with the majority of real systems where diffusion takes place in the transition region while the diffusion coefficients are functions of concentrations of individual species¹. The general expression for the flux of a multicomponent mixture in a porous medium must then incorporate, apart from the adequate expression for the diffusional flux, also a term representing the contribution of the forced (Darcy) flow due to the pressure gradient within the pores¹⁻³. Solution of such differential mass balances with general flow terms is naturally difficult. From this standpoint it is important to explore possible avenues for a simplification of the complete model in order to reduce the set of balance equations to a form facilitating numerical solution

The aim of this work, relating to our previous communication², has been to assess the effect of the forced flow and single out conditions under which this contribution may be neglected.

The Mass Balance in a Catalyst Particle

A general q -component system supporting the set of m reactions may be described under the steady and isothermal conditions by the set of differential equations which in the direction of *e.g.* z axis takes the form

$$d\mathbf{N}/dz = \mathbf{a}\mathbf{r} . \quad (1)$$

The flux of a multicomponent mixture in an isothermal medium may be expressed generally as a sum of the contributions of the diffusional flux and the forced flow

$$\mathbf{N} = \mathbf{N}^d + \mathbf{N}^f \quad (2)$$

i.e. after substituting for individual contributions² by

$$\mathbf{N} = -c \mathbb{D}(d\mathbf{y}/dz) - \mathbf{y}\mathbf{B}(dc/dz) . \quad (3)$$

The matrix of effective diffusional coefficients \mathbb{D} is defined by

$$\mathbb{D} = \mathbf{F}^{-1} . \quad (4)$$

The meaning of the inverse matrix \mathbf{F} becomes clear from the following equation

$$-c(d\mathbf{y}/dz) = \mathbf{F}\mathbf{N}^d , \quad (5)$$

representing a matrix notation of the set of differential equation for steady state diffusion of a multicomponent mixture in the transition region in a isothermal and isobaric particle. The elements of the matrix \mathbf{F} for diffusion in the transition region are defined⁴ by Eqs (6) and (7)

$$F_{ij} = - \frac{y_i}{(\varepsilon/\tau) \mathcal{D}_{ij}} , \quad i \neq j \quad (6)$$

$$F_{ii} = \frac{1}{(\varepsilon/\tau) \mathcal{D}_{\kappa i}} + \sum_{\substack{l=1 \\ l \neq i}}^q \frac{y_l}{(\varepsilon/\tau) \mathcal{D}_{li}} . \quad (7)$$

The form of these equations originates from the model of a bundle of equal-radius capillaries with adjustable parameters R and (ε/τ) .

Symbol \mathbf{y} in the second term on the right hand side of Eq. (3), expressing the contribution of the forced flow, is a diagonal matrix of mole fractions of a gas mixture and \mathbf{B} is a vector of permeability coefficients⁵. These coefficients are generally functions of the mean pore diameter R , pressure P and mole fractions y_i .

On expressing the flow term from Eq. (3) the set of balance equations takes the following form

$$d/dz(-c \mathbb{D} d\mathbf{y}/dz - \mathbf{yB} dc/dz) = \mathbf{ar}. \quad (8)$$

The mole fractions of individual species are further constrained by

$$\sum_{i=1}^q y_i = 1. \quad (9)$$

The set of Eqs (8) and (9) is then solved with the boundary conditions

$$\begin{aligned} z = L \quad y_i &= y_{is} \\ c &= c_s \quad i = 1, 2, \dots, q \\ z = 0 \quad dy_i/dz &= 0 \end{aligned} \quad (10)$$

for $(q + 1)$ unknowns y_i ($i = 1, 2, \dots, q$) and c .

Clearly, solution of this boundary value problem, which owing to the form of the left hand side of Eq. (8) is considerably complicated, could be considerably facilitated if the contribution of the forced flow were neglected while still satisfying the constraint (9). In such case the description of the flow of the reaction mixture would reduce to the diffusional contribution while the overall concentration c could be regarded constant along the pore length. In case of validity of Eq. (9) one equation in the set (5), describing diffusion of a multicomponent reaction mixture is always a linear combination of the others. The determinant of the matrix \mathbf{F} then vanishes and corresponding inverse matrix \mathbb{D} of the diffusional coefficients cannot be found. The boundary value problem (8)–(10) changes under such conditions to a simultaneous solution of $(q - 1)$ independent equations of the set (5).

$$-c dy_i/dz = \sum_{j=1}^{(q-1)} F_{ij} N_j, \quad i = 1, 2, \dots, (q - 1) \quad (11)$$

with the balance equations, which for a catalyst in the form of an infinite slab may be written as

$$dN_j/dz = \sum_{k=1}^m a_{jk} r_k, \quad j = 1, 2, \dots, (q - 1). \quad (12)$$

The boundary conditions for the solution of the set (11)–(12) are as follows

$$\begin{aligned} z = L \quad y_i &= y_{is} \\ z = 0 \quad N_j &= 0 \quad i, j = 1, 2, \dots, (q - 1) \end{aligned} \quad (13)$$

Concentration of the remaining q -th component is fixed by the constraint (9). Further, $(q - m)$ fluxes of non-key components may be eliminated from the set (11)–(13) using stoichiometric relations to express these fluxes as functions of m key components. The functional relationship is

$$\mathbf{N}^n = \mathbf{a}^n(\mathbf{a}^k)^{-1} \mathbf{N}^k, \quad (14)$$

where \mathbf{N}^k and \mathbf{N}^n stand for the parts of the flux vector $\mathbf{N} = (N_1, N_2, \dots, N_q)^T$, containing the fluxes of the key and the non-key components

$$\mathbf{N}^k = (N_1, N_2, \dots, N_m)^T \quad (15)$$

$$\mathbf{N}^n = (N_{m+1}, \dots, N_q)^T \quad (16)$$

Analogously, \mathbf{a}^k and \mathbf{a}^n are parts of the matrix of stoichiometric coefficients containing the coefficients of the key and the non-key components².

Conditions for Neglecting the Forced Flow

Conditions (9) may be written in a differential form as

$$\sum_{i=1}^q dy_i/dz = 0. \quad (17)$$

From the Stefan–Maxwell relations for the diffusional flux (5) it is apparent that in order to satisfy the last equation we must have

$$\sum_{j=1}^q N_j \sum_{i=1}^q F_{ij} = 0. \quad (18)$$

Since generally we have $N_j \neq 0$ there follows from Eq. (18) that the constraints (9) or (17) are equivalent to

$$\sum_{i=1}^q F_{ij} = 0, \quad (19)$$

or, after expressing F_{ij} from the definitions (6) and (7) to

$$1/D_{\mathbf{K}j} = 0. \quad (20)$$

The last equation holds accurately only in the region of continuum, where $D_{\mathbf{K}j} \rightarrow \infty$. In a porous medium, where $D_{\mathbf{K}j}$ assumes always finite values, Eq. (20) is never

fulfilled precisely. Thus, generally speaking, the contribution of the forced flow in a porous medium can never be neglected, not even in region of molecular diffusion, where only $1/D_{Kj} \ll D_{ij}$. It may be expected though that conditions exist when the contribution of the forced flow to the net flow of the reaction mixture is negligible from the practical point of view. It thus seems practicable to find such conditions.

If in the description of the flow of a multicomponent mixture through a porous medium the contribution of the forced flow is unjustly neglected, the sum of mole fractions of individual species in an arbitrary point of a porous medium, obtained by solving the simplified balance equations, deviates from unity. Provided the pressure gradient within the pores is not large, it may be anticipated¹ that the forced flow induced by this gradient is proportional to the deviation of the sum of mole fractions from unity $(1 - \sum_{i=1}^q y_i)$. For a given heterogeneous catalytic reaction the quantity $(1 - \sum_{i=1}^q y_i)$ provides a measure of the effect of the contribution of the forced flow and eventually a criterion for the conditions under which the effect of the forced flow may be safely neglected.

Assessment of the Effect of the Forced Flow on a Consecutive Heterogeneous Catalytic Reaction

The calculation of the concentration profiles prevailing in a catalyst particle supporting a reaction may be based on Eqs (11)–(13), which, however, must be formulated for all q components for we cannot assume validity of Eq. (9) *a priori*. As noted, the deviation of the sum of computed mole fractions of individual species from unity is a measure of the error committed by neglecting the pressure gradient in the porous particle. This error depends firstly on the mean pore diameter of the catalyst and on the ratio of the reaction rate constants of individual reactions. To illustrate the situation a model reaction has been chosen exhibiting a change of the number of moles while the species diffusing in the porous medium have different molecular weights. These features has *e.g.* consecutive trimerisation of ethylene following the scheme



In this system we have chosen A_1, A_2 for the key components. The balance equations (12) for the fluxes of the key components and the stoichiometric relationship (14) for the non-key component A_3 may be written for the schemes (A) and (B) as

$$dn_1/dx = -M^2(2q_1 + q_2) \quad (21)$$

$$dn_2/dx = M^2 q_2 \mathcal{D}_{K1}/\mathcal{D}_{K2} \quad (22)$$

$$n_3 = -(0.5n_1 \mathcal{D}_{K1}/\mathcal{D}_{K3} + 1.5n_2 \mathcal{D}_{K1}/\mathcal{D}_{K2}), \quad (23)$$

Eqs (21)–(23) are dimensionless; the dimensionless flux is $n_i = LN_i/cD_{K1}$, the Thiele modulus $M = L\sqrt{r_{1s}/cD_{K1}}$, $x = z/L$, the dimensionless rate equations $q_i = r_i/r_{1s}$. After substitution $r_1 = k_1y_1$, $r_2 = k_2y_1y_3$ and the ratio of the Knudsen diffusion coefficients $\mathcal{D}_{K1}/\mathcal{D}_{K3} = \sqrt{2}$, $\mathcal{D}_{K1}/\mathcal{D}_{K2} = \sqrt{3}$ we obtain

$$dn_1/dx = -M^2y_1(2 + y_3/s)/y_{1s} \quad (24)$$

$$dn_2/dx = M^2y_1y_3\sqrt{(3)/s}y_{1s} \quad (25)$$

$$n_3 = -(0.5\sqrt{(2)}n_1 + 1.5\sqrt{(3)}n_2), \quad (26)$$

where the selectivity coefficient, s , has been defined as the ratio of the rate constants of both reactions, namely $s = k_1/k_2$. The diffusion equation (11) for all species of the reaction system in the dimensionless form reads

$$dy_1/dx = -(n_1 + \Delta_1n_1y_2 - \Delta_2n_2y_1 + \Delta_3n_1y_3 - \Delta_4n_3y_1) \quad (27)$$

$$dy_2/dx = -(n_2 + \Delta_2n_2y_1 - \Delta_1n_1y_2 + \Delta_5n_2y_3 - \Delta_6n_3y_2) \quad (28)$$

$$dy_3/dx = -(n_3 + \Delta_4n_3y_1 - \Delta_3n_1y_3 + \Delta_6n_3y_2 + \Delta_5n_2y_3), \quad (29)$$

where Δ_i designates the ratios of the Knudsen and the binary diffusion coefficients, $\Delta_1 = \mathcal{D}_{K1}/\mathcal{D}_{12}$, $\Delta_2 = \mathcal{D}_{K2}/\mathcal{D}_{12}$, $\Delta_3 = \mathcal{D}_{K1}/\mathcal{D}_{13}$, $\Delta_4 = \mathcal{D}_{K3}/\mathcal{D}_{13}$, $\Delta_5 = \mathcal{D}_{K2}/\mathcal{D}_{23}$, $\Delta_6 = \mathcal{D}_{K3}/\mathcal{D}_{23}$. The initial and the boundary conditions are

$$\text{for } x = 0, n_1 = n_2 = n_3 = 0 \quad (30)$$

$$\text{for } x = 1, y_{1s} = \pi_1, y_{2s} = \pi_2, y_{3s} = \pi_3, \quad (31)$$

The calculation of mole fractions in a particle from Eqs (24)–(29) with the boundary conditions (30) and (31) represents a boundary value problem for the set of ordinary first-order non-linear differential equations. This set was solved by the shooting method⁶. Profiles of mole fractions were computed for various mean pore diameters and various selectivity factors, s , at constant composition of the ambient reaction mixture: $y_{1s} = 0.9$, $y_{2s} = 0.004$ and $y_{3s} = 0.096$, and are shown in Figs 1 and 2. The figures show also the deviations of the sum of mole fractions $\sum y_i$ from unity. It is apparent that maximum deviations occur in particle's center, i.e. at $x = 0$ for in this point the neglected pressure gradient becomes manifest most. In narrow pores with prevailing Knudsen type diffusion the deviations of $\sum y_i$ from unity are largest,

which is in accord with Eq. (19). In this case it is permissible to neglect the terms containing ratios of the diffusion coefficients Δ_i in Eqs (27)–(29) for $\Delta_i \rightarrow 0$. These equations thus change to ones analogous to the Fick law. For the same mean pore diameter the error committed by neglecting the forced flow may be influenced by the selectivity factor, s . If the rate of the first reaction is much higher than that of the second, *i.e.* for high s , the deviations from unity are smaller as the magnitude of the pressure gradient in the particle influences only the first reaction (A) with a smaller mole change than that corresponding to the overall trimerisation (A) and (B). The

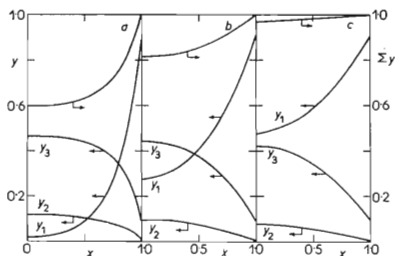


FIG. 1

Mole Fraction Profiles in a Catalyst Particle; Effect of Mean Pore Radius

$s = 2.5$; $a M^2 8.715$, $R 5$ nm; $b M^2 0.8715$, $R 50$ nm; $c M^2 0.08715$, $R 500$ nm.

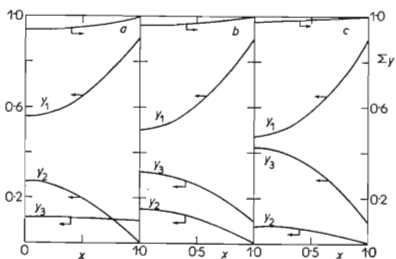


FIG. 2

Mole Fraction Profiles in a Catalyst Particle; Effect of Selectivity Factor

$R 500$ nm, $M^2 0.08715$; $a s 0.25$; $b s 1$; $c s 2.5$.

magnitude of the quantity $1 - \sum y_i$, calculated for the point $x = 0$ for various mean pore radii and selectivity factors, s , is shown in Table I. From this table it is apparent that the deviations $1 - \sum y_i$, independently of the selectivity, are considerable even in catalysts with relatively wide pores (50 nm) typical for commonly used catalysts. Only extremely large pores (500 nm) exhibit negligible deviations of the sum of mole fractions from unity.

In the derivation of the balance equations it was assumed that mole fractions of the three components were mutually independent. Setting aside Eq. (9) from the balance set permitted on the one hand assessment of the error committed by neglecting the forced flow, but, on the other hand, lead to incorrect values of the effectiveness factor. While the errors due to neglected forced flow show mostly in narrow pores, the errors in the effectiveness factor, committed by omitting Eq. (9), become manifest most in wide pores as the terms with Δ_i on the right hand sides of Eqs (27)–(29) play a role increasingly large with R . On defining the effectiveness factor as the integral mean of the true reaction rate divided by the reaction rate at the conditions prevailing on particle's surface, the expression for the effectiveness factors of the reactions (A) and (B) may be computed from

$$\eta_1 = \frac{\int_0^1 r_1(x) dx}{r_{1s}} = \int_0^1 \varrho_1(x) dx \quad (32)$$

$$\eta_2 = \frac{\int_0^1 r_2(x) dx}{r_{2s}} = \frac{s}{y'_{2s}} \int_0^1 \varrho_2(x) dx \quad (33)$$

The effectiveness factors of reactions (A) and (B), computed from these relations for the mean pore diameter $R = 5$ nm and the selectivity factor $s = 2.5$ (Table I) are

TABLE I

Deviations of the Sum of Mole Fractions from Unity ($1 - \sum y_i$) for Various Mean Pore Radii and Selectivity Factors at $x = 0$

R , nm	s			
	0.25	1.0	1.43	2.5
5	—	0.509	0.469	0.407
50	—	0.251	—	0.186
500	0.058	0.040	—	0.027

$\eta_1 = 0.226$ and $\eta_2 = 0.758$. These values may be regarded as correct because in narrow pores the balance equations (24)–(26), together with the diffusion equations degenerated to the Fick law (for $\Delta_i \rightarrow 0$), formally describe the limiting case of the complete balance incorporating both the diffusional and forced flow within the particle. Substituting the mole fractions in Eqs (24)–(26) by molar concentrations c_i , these equations correspond to the balances (8) in the Knudsen region and the resulting concentration profiles are identical with the profiles of mole fractions calculated *e.g.* in Fig. 1a. The farther away from the Knudsen region the greater the error involved in the computed mole fraction profiles and the effectiveness factors computed from these profiles using the definition equations (32) and (33).

The results of this work have confirmed that in real systems supporting heterogeneous catalytic reactions the general balance (2) should be used. The pressure gradient within the particle affects the mole fractions profiles less in catalysts with larger pores and with higher selectivity factor. Nevertheless, it is not possible to ascertain whether the neglected forced flow shall cause considerable errors in the balances.

LIST OF SYMBOLS

a_{ij}	stoichiometric coefficient of component A_i in the j -th reaction, element of matrix a
A_i	components of the reaction mixture
B_i	permeability of individual components, element of vector B
c	total concentration
c_i	molar concentration
D	matrix defined by Eq. (4)
\mathcal{D}_{ij}	binary diffusion coefficient
\mathcal{D}_{Ki}	Knudsen diffusion coefficient dependent on R
F_{ij}	elements of matrix F
L	characteristic particle size
M	Thiele modulus
m	number of reactions
N_i	flux of individual species, element of vector N
n_j	dimensionless flux
q	number of components of the system
R	mean pore radius
r_j	rate of the j -th reaction, element of vector r
s	selectivity factor
x	independent variable
y_i	mole fraction, element of vector or diagonal matrix y
z	coordinate

Δ_i	dimensionless coefficient
ε	porosity
η_j	effectiveness factor of j -th reaction
ϱ_j	dimensionless rate of j -th reaction
τ	tortuosity
π_i	mole fraction on the surface

Subscripts

i, j, l	components
s	surface value
d	diffusional (flux)
f	forced (flux)
k	key (flux)
n	non-key (flux)

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