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APPLICABILITY OF LINEARIZED DUSTY GAS MODEL FOR MULTICOMPONENT DIFFUSION OF GAS MIXTURES IN POROUS SOLIDS

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The transport of gaseous components through porous media could be described according to the well-known Fick model and its modifications. It is also known that Fick's law is not suitable for predicting the fluxes in multicomponent gas mixtures, excluding binary mixtures. This model is still frequently used in chemical engineering because of its simplicity. Unfortunately, besides the Fick's model there is no generally accepted model for mass transport through porous media (membranes, catalysts etc.). Numerous studies on transport through porous media reveal that Dusty Gas Model (DGM) is superior in its ability to predict fluxes in multicomponent mixtures. Its wider application is limited by more complicated calculation procedures comparing to Fick's model. It should be noted that there were efforts to simplify DGM in order to obtain satisfactory accurate results.

In this paper linearized DGM, as the simplest form of DGM, is tested under conditions of zero system pressure drop, small pressure drop, and different temperatures. Published experimental data are used in testing the accuracy of the linearized procedure. It is shown that this simplified procedure is accurate enough compared to the standard more complicated calculations.

KEYWORDS: Dusty Gas Model, Multicomponent diffusion, Porous solids

INTRODUCTION

The industrial application of porous solids is quite widespread. They are used as heterogeneous catalysts, adsorbents, membranes etc. Additionally, the porous electrodes are used in fuel cells technology. Besides extensive experimental work there are numerous models concerning porous solid properties and multicomponent transport (1).

It should be noted that there is no generally accepted model for multicomponent diffusion through porous solids (2). Some of them belong to the group called continuum models.

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They are relatively easy to use and sufficiently accurate if a porous medium does not change its textural properties. However, they are not well suited if noticeable changes in the pore connectivity, pore plugging and fragmentation occur (2).

Certain progress has been made in the last years employing discrete models based on the network representation of porous medium (2). Unfortunately, the application of the discrete models, (pore network models) requires tremendous computation time if transport should be treated realistically. This is their major shortcoming.

Concerning continuum models, the modified Fick’s law is the simplest diffusion model and it is often used for dilute or binary systems. It is also well-known about its drawbacks for multicomponent systems (3). In order to describe multicomponent diffusion more accurately, models based on Maxwell-Stefan equations are preferred and recommended (3, 4, 5). Main obstacles of these models application are more complicated calculation procedures comparing to the Fick's approach. Therefore, any justified simplifications of the models or calculation procedures would be acceptable.

Today, there are three most frequently used models available for description of combined transport of multicomponent gaseous mixtures through porous solids: the Dusty Gas Model (DGM), the Mean Transport Pore Model (MTPM), and the Binary Friction Model (BFM) (6). These models are based on Maxwell-Stefan description of multicomponent diffusion in pores and on the d'Arcy equation for permeation.

The aim of this study was to analyze the application of the simplified procedure for transport parameters determination in porous solids, based on the linearization of the Dusty Gas model (7). This procedure was tested using the published experimental data (3,7).

EXPERIMENTAL

Flux models through porous solids

Modified Fick's model represents the combination of three transport mechanisms: bulk diffusion, Knudsen diffusion and viscous flow. Fick's model defines component flux as a product of diffusion coefficient and partial pressure (concentration) gradient of the particular component:

$$N_i^D = -\frac{D_i^e}{RT}\nabla(x_i P),\ i = 1,\dots,n \qquad [1]$$

In small pores, the molecule-wall interactions are determining the process (Knudsen diffusion), and in free space, molecule-molecule interactions (bulk diffusion). In each of these two regimes diffusion coefficients have different values. In the transition region it is common to use the Bosanquet formula in order to evaluate the diffusion coefficient, while in bulk diffusion region Wilke equation is most commonly used (3).

When a convective transport contributes to the total transport, d'Arcy equation of viscous flow can be added, resulting in what is known as extended Fick's model for porous media:

$$N_i = N_i^D + N_i^V,\quad N_i = \frac{1}{RT}\left(D_i^e\nabla(x_i P) + \frac{B_0 x_i P}{\mu}\nabla P\right),\quad i = 1,\dots,n \qquad [2]$$

This equation is frequently used primarily because the component flux is expressed in terms of concentration and pressure gradients. Methods of solving these equations will not be discussed here. The simplest case is one dimensional problem where gradients are replaced by finite differences (linear form):

$$N_i = \frac{\overline{P}}{RT}\left(D_i^e \Delta x_i + \frac{B_0 \overline{x}_i}{\mu} \Delta P \right), \quad i = 1,...,n \qquad [3]$$

Contrary to the Fick's law for multicomponent diffusion concerning molecule to molecule interactions, the more correct and theoretically based model is given by Maxwell-Stefan diffusion equations.(3). The diffusive flux of component (in this concept) is given by the extended Maxwell-Stefan equation, which includes both, the bulk and the Knudsen diffusion mechanisms:

$$\frac{1}{RT}\nabla\left(Px_i\right) = \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_i N_j^D - x_j N_i^D}{D_{i,j}^e} - \frac{N_i^D}{D_{iK}^e} \qquad [4]$$

According to the Dusty Gas model (DGM) of diffusive transport total flux is obtained by adding convective (viscous) contributions, similar as in equation [2]. The following formulation of DGM is often used as working equation in experimental investigation and in modelling of multicomponent gas transport processes in general.

$$\frac{P}{RT}\nabla x_i + \frac{x_i}{RT}\left(1 + \frac{B_0 P}{\mu D_{iK}^e} \right)\nabla P = \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_i N_j - x_j N_i}{D_{i,j}^e} - \frac{N_i}{D_{iK}^e}, \quad i = 1,...,n \qquad [5]$$

There are *n* independent equations, *n* independent fluxes, N_i and, *n* independent gradients $\nabla x_1,...,\nabla x_{n-1},\ \nabla P$.

In order to solve or use DGM equations an extensive effort is needed, excluding some special cases.(4,5). DGM equations fluxes are not given explicitly comparing to extended Fick's model, therefore, simplification of the calculation procedure would be very useful. Above derived equations of multicomponent transport refer to macro and meso-porous solids.

The common approximation is to consider one dimensional problem:

$$\frac{P}{RT}\frac{dx_i}{dz} + \frac{x_i}{RT}\left(1 + \frac{B_0 P}{\mu D_{iK}^e} \right)\frac{dP}{dz} = \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_i N_j - x_j N_j}{D_{i,j}^e} - \frac{N_j}{D_{iK}^e}, \quad i = 1,...,n \qquad [6]$$

with the following boundary conditions :

$$z = 0,\ x_i(0) = x_i^0,\ P(0) = P^0; \quad z = \delta,\ x_i(\delta) = x_i^\delta,\ P(\delta) = P^\delta \qquad [7]$$

and the additional constraints :

$$\sum_{i=1}^{n} x_i = 1;\ \frac{dN_i}{dz} = 0,\ i = 1,...,n \qquad [8]$$

From the composition constraint follows that only *n-1* molar fluxes (gradients) are independent and by summing the equations [6] the following equation for total pressure gradient is obtained:

$$RT\sum_{i=1}^{n}\frac{N_i}{D_{iK}^e} = -\left(1 + \frac{B_0 P}{\mu}\sum_{i=1}^{n}\frac{x_i}{D_{iK}^e} \right)\cdot\frac{dP}{dz} \qquad [9]$$

The constraint of zero component flux gradients is valid when there are no chemical reactions. The equations [6] with the constraints [8] represent a system of $2n+1$ equations with $2n$ unknowns (n compositions, pressure, n fluxes).

Solving these equations in order to obtain concentration and pressure profiles requires initial estimates of all the fluxes N_i ($i=1,..n$). Thus, the procedure includes finding the appropriate component fluxes which satisfy the resulting system of ordinary differential equations. It is carried out numerically in the general case, though analytical solutions have been given for some very special cases. (3, 4, 5). Summing over the n species with the constraint of absence of total pressure gradient DGM equations results as $\sum_{i=1}^{n} N_i M_i^{1/2} = 0,$ which represents the generalized Graham's law. On the contrary, modified Fick's low would define the equimolar diffusion as $\sum_{i=1}^{n} N_i = 0$.

A convenient simplified procedure for the solution of DGM can be developed as in reference (7).

The fluxes can be calculated explicitly with an assumption of linear profiles of composition and total pressure along the diffusional path. With these assumptions driving force is as follows:

$$d_i = \frac{\Delta x_i}{\Delta z} + \bar{x}_i \left(1 + \frac{B_0 \bar{P}}{\mu D_{iK}^{e}} \right) \frac{\Delta P}{\bar{P} \Delta z} \qquad [10]$$

where :

$$\Delta x_i = x_i^{\delta} - x_i^{0}, \bar{x}_i = \frac{x_i^{\delta} + x_i^{0}}{2},\ i = 1,...,n,\ \Delta P = P^{\delta} - P^{0},\ \bar{P} = \frac{P^{\delta} + P^{0}}{2}, \Delta z = z^{\delta} - z^{0} \qquad [11]$$

This linear form of DGM equation [17] yields the values of the n fluxes explicitly.

RESULTS AND DISCUSSION

Testing of linear DGM (linear, nonlinear, exact)

Given linear representation, [11], could be considered as the simplest form of DGM (4, 5, 7). Linear DGM is tested against published experimental data for binary and ternary gas mixtures including ideal and non-ideal behaviour (7).

Authors generally used the DGM in the form of the system of first order linear equation ODE, [5]. This system is solved numerically as a boundary value problem (nonlinear problem in the following text). Initial estimates of component fluxes were obtained by using the linear DGM. Analytical solution in some cases could be found („exact“ solution in the following text) when DGM is represented with a linear ODE (3). In order to test all of these forms (linear, non-linear, „exact“) of DGM numerical simulation was performed (3,7).

The used gas mixture consisted of Ar, He, N_2 and H_2 in order to avoid adsorption effects on pores surface and possible effect of surface diffusion (which is not included in DGM). Binary Fick's diffusion coefficients are calculated by Fuller-Shettler-Giddings correlation (9). The usual experimental conditions are assumed $P = 101.325\,kPa$, T=298K. Characteristics of porous solid are given elsewhere (7).

Numerical simulation is performed for different ternary combination of the above mentioned gases. Typical numerical results obtained for net flux through porous solids are given in the Table 1. Binary mixture on one side (Ar + N_2) with given mole fraction of Ar (x_{Ar}^0) and pure component (H_2) on the other side of the porous solid ($x_{H_2}^{\delta} = 1$). The results are for zero pressure drop across the porous solid ($\Delta P = 0$).

Table 1. Net fluxes ($N = \sum N_i$) for different forms of DGM models

Mole fraction- x_{Ar}^0	Net fluxes - $N \times 10^2$ $\left[\frac{mol}{m^2 s}\right]$		
	Linear DGM	Non-linear DGM	„Exact“ DGM
0.9	-2.3	-2.4	-2.3
0.8	-2.0	-2.0	-2.0
0.7	-1.6	-1.6	-1.8
0.6	-1.2	-1.2	-
0.5	-0.8	-0.8	-
0.4	-0.4	-0.4	-
0.3	0.1	0.1	-
0.2	0.6	0.6	-
0.1	1.1	1.1	-

Results from all other combinations of gases and compositions in ternary mixtures are not given because the same conclusions could be made; also negligible difference between results of linear and non-linear DGM was noticed. Although the analytical solution (if exists) is more preferred than the numerical solution, in this case, to solve the governing system of linear first order ODE analytically, some of numerical methods for matrix algebra must be employed. These numerical procedures often fail to converge which was the main reason why exact solution could not be found (3). Therefore, focus will be only on linear and non-linear solutions of DGM.

In Fig.1 typical composition profiles across the porous solid for all the analyzed models are given, Ar-H_2 binary mixture on one side, and the pure component He on the other side of the porous solid, for linear ($N_{Ar} = 9.5 \cdot 10^{-3}, N_{H_2} = 0.014, N_{He} = -0.04$), non-linear ($N_{Ar} = 9.6 \cdot 10^{-3}, N_{H_2} = 0.014, N_{He} = -0.04$) and exact form of DGM ($N_{Ar} = 0.011, N_{H_2} = 0.019, N_{He} = -0.05$).

Although, only the linear DGM uses the assumption of linear composition profiles, linear composition profiles are also always obtained for both, non-linear and exact (when solution is found) DGM.

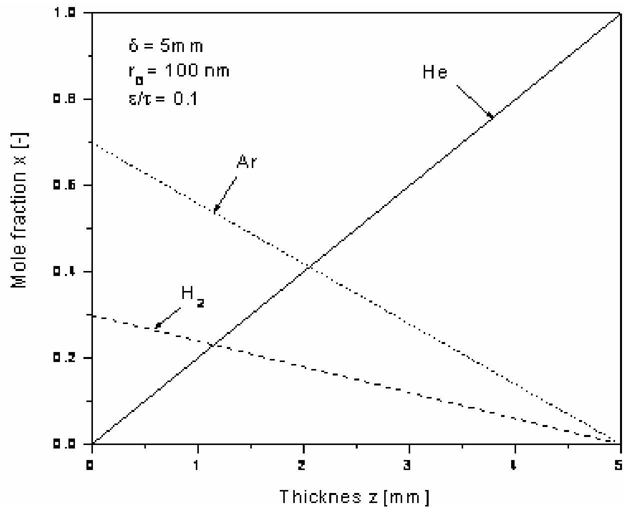

Fig 1. Composition profiles in ternary mixture (Ar-H_2-He)

Influence of pressure drop

The influence of pressure drop, $\Delta P \neq 0$, has been studied also. The analysis is based on the reference and data for ternary mixture from (7, Table 1, Table 2). In reproducing results from the literature denoted „exact" solutions coincide with results obtained by the non-linear procedure given here. Although in the reference (7) experimental and simulated data have been analyzed only for zero pressure drop, analysis has been extended by including the total pressure difference. As the experimental results were not available in that case, this analysis has been restricted to the comparison the linear and non-linear models.

Pressure difference has been applied to the mentioned data and it was observed as the deviation from mean pressure. The mean pressure was kept constant and the ratio of pressure difference and mean pressure was calculated as $\Delta P = c \cdot \overline{P}$, where the constant c could be arbitrarily chosen. The comparison between linear and nonlinear models was performed by the calculating the accompanied component fluxes. The ratio of component fluxes, $R_{Ni} = \left| \frac{N_i^{\text{ln}} - N_i^{\text{nln}}}{N_i^{\text{nln}}} \right|$ was chosen as an indication of model differences.

In Fig.2. values of the flux ratios for different c values and the case of ternary mixture (He, Ne, Ar) are presented. At $\Delta P = 0$ the fluxes were N_{He}~-0.5, N_{Ne}~0.12, N_{Ar}~0.07. When $\Delta P = 0$ ($c = 0$) the difference between models is negligible. This is in accordance with previous discussion.

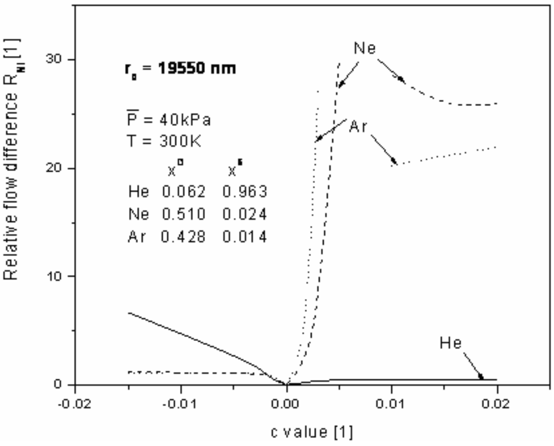

Fig 2. The comparison of linear and nonlinear DGM for different pressure difference ($B_0=r_0^2/8$, $\varepsilon/\tau=1$, $\mu=22.6\times10^{-6}$ *Pa s*, $\delta=9.6$*mm*)

The difference between models will increase with increase of ΔP. Positive ΔP will aid the flux of He and counter the fluxes of Ne, Ar and negative ΔP will have the opposite influence. When the flux of component is high and additionally contributed by pressure difference the relative difference between models will be lower (He - negative flux, positive ΔP).

In the case of lower fluxes especially when they are suppressed by pressure difference (Ne, Ar - positive flux, positive ΔP) the relative difference between models is more noticeable. Additionally, if the ΔP is high enough the sign of the flux could change. In this case, the fluxes of Ne and Ar changed from positive to negative. This could be noted as the vertical asymptote (break for Ne, Ar in Fig 2.) for *c* values between 0.005 and 0.01 because in this regime there is a *c* value where the fluxes calculated by nonlinear model are equal to zero.

In the case of negative ΔP and comparing to positive ΔP, the model differences in fluxes for He (He - negative flux, negative ΔP) are greater and for Ne, Ar (Ne,Ar – positive flux, negative ΔP) are significantly lower. Nonlinear procedure could fail for large pressure difference (greater absolute *c* values) i.e. the system could become stiff and therefore much difficult to solve. In the range of *c* values, presented in Fig.2., used numerical procedure converged, and outside of this region it failed.

Influence of temperature

It is also important to investigate the temperature influence, especially for the elevated temperatures (porous catalysts, fuel cell (SOFC) electrodes etc.). The used experiments (7) are performed on 27 °C. Fig. 3 represents the temperature influence and the simulation for the data from the same experiment. It could be seen that the difference in predicting the component flows between two models is lower at higher temperatures. DGM is also used in analysis of the transport through the porous electrodes in a fuel cell system, SOFC (12). The operating temperatures of SOFC are very high (~527-727 °C).

Although the authors applied nonlinear two-dimensional DGM they assumed the linear concentration and pressure gradients. The authors also justified this assumption over a large range of electrode structures and fuel cell operating conditions. This also implies the use of linear instead of nonlinear models.

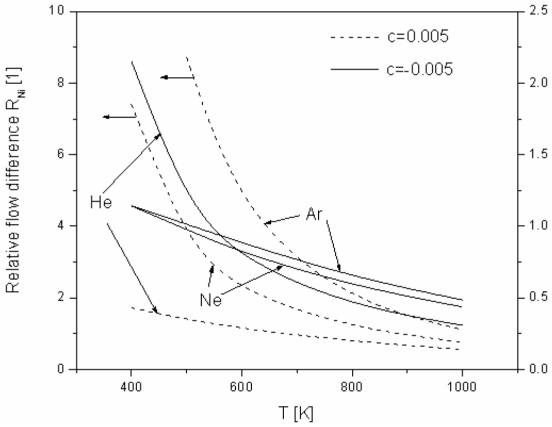

Fig 3. The comparison of linear and nonlinear DGM for different temperatures

CONCLUSION

In general, the difference between the compared models can be considered acceptable for zero or smaller pressure difference. On the other hand when the significant pressure difference is applied, linear model is quite acceptable for smaller mean pore radius. Considering the temperature, the analysis indicates that the linear model is more useful when the temperatures are higher.

Therefore, it could be concluded that for isothermal multicomponent diffusion the linear DGM model with its advantage of simplicity can be used without significant loss of accuracy for zero ΔP (or small deviation from zero), smaller mean pore radius and higher temperatures.

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ПРИМЕЊИВОСТ ЛИНЕАРИЗОВАНОГ ДАСТИ ГАС МОДЕЛА НА МУЛТИКОМПОНЕНТНУ ДИФУЗИЈУ ГАСНИХ СМЕША КРОЗ ПОРОЗНИ МЕДИЈУМ

Јелена Марковић, Радован Оморјан

Транспорт гасова кроз порозони медијум може се описати добро познатим Фиковим законом као и неким његовим модификацијама. Познато је да Фиков закон није погодан за предвиђање флуксева у мултикомпонентној гасној смеши, са изузетком бинарних смеша. Међутим овај модел се и даље често користи у хемијском инжењерству због његове једноставности. Нажалост, осим Фиковог модела не постоји ниједан опште прихваћен модел за пренос масе кроз порозни медијум (мембране, катализаторе и сл.). Бројне студије о преносу масе кроз порозни медијум показале су да се помоћу Дасти гас модела (ДГМ) знатно боље могу предвидети флуксеви када се ради о мултикомпонентној смеши. Шира примена ДГМ ограничена је веома компликованим поступцима за израчунавање у поређењу са Фиковим моделом. Управо зато је пожељно доћи до једноставнијег облика ДГМ који би ипак дао довољо тачне резулате.

У раду је испитиван линеаризовани облик ДГМ, као његов најједноставнији облик, у условима без пада притиска система, када постоји мали пад притиска, као и за различите средње пречнике пора и различите температуре. Приликом тестирања

коришћени су експериментални подаци из литературе. Показано је да поједностављени облик ДГМ-а даје довољно тачне резулате у поређењу са компликованијим облицима истог модела.

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