Gas-Phase Diffusion in Porous Media: Comparison of Models

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ABSTRACT

Two models are commonly used to analyze gas-phase diffusion in porous media in the presence of advection, the Advective-Dispersive Model (ADM) and the Dusty-gas Model (DGM). The ADM, which is used in TOUGH2, is based on a simple linear addition of advection calculated by Darcy's law and ordinary diffusion using Fick's law with a porosity-tortuosity-gas saturation multiplier to account for the porous medium. Another approach for gas-phase transport in porous media is the Dusty-Gas Model. This model applies the kinetic theory of gases to the gaseous components and the porous media (or "dust") to combine transport due to diffusion and advection that includes porous medium effects. The two approaches are compared in this paper.

INTRODUCTION

Gas-phase diffusion in porous media may be significant in the flow of multiphase fluids and the transport of contaminants in the subsurface. In many applications, such as removal of nonaqueous phase liquid (NAPL) contaminants from low-permeability layers in the subsurface, gas-phase diffusion may be the limiting transport mechanism. Gas-phase diffusion may also be important in the analysis of contaminant migration in potential nuclear waste repositories, evaporation and drying processes, and porous catalysts.

A number of different models for combined advection-diffusion of gases in porous media have been employed that are strongly correlated with the corresponding discipline. For example, in earth sciences and in many engineering fields, the most widely used model is the Advective-Dispersive Model, or ADM. In chemical engineering, the most common approach for gas-phase transport in porous media is the Dusty-Gas Model. These models are dramatically different in their treatment of gas-phase diffusion. The main objectives of the present paper are to compare the ADM and DGM models with Graham's laws, which are fundamental relationships for diffusion, and to evaluate both models against a number of comprehensive experimental data sets. In addition, the two approaches are applied to an air-water heat pipe that is encountered in earth science applications.

DIFFUSION MODELS

Advective-Dispersive Model

The Advective-Dispersive Model (ADM) is commonly used in earth sciences as exemplified by TOUGH2 (Pruess, 1991). The ADM is based on a simple *ad hoc* linear addition of advection calculated by Darcy's law and ordinary diffusion using Fick's law. Slip effects, or Knudsen diffusion, are included through a Klinkenberg parameter to define an effective permeability for the advective flux. Porous medium effects for ordinary diffusion are included through a porosity-tortuosity-gas saturation factor applied to the diffusive flux in free space. This simple additive approach, while intuitively appealing, ignores possible coupling between advection and diffusion.

The ADM mass flux for gas-phase component i, F_i, in a binary mixture is

$$F_i = -k \frac{k_{r,g}}{\mu_g} \rho_g \omega_i \left(\nabla P_g - \rho_g g_c \right) - D_{12} \rho_g \nabla \omega_i \quad (1)$$

where $D_{12} = D_{21}$ is assumed. Slip, or Knudsen diffusion, is simply incorporated into the model through the Klinkenberg factor, b, or

$$k = k_o \left(1 + b/P_g \right) \quad (2)$$

The effective diffusion coefficient is given by

$$D_{12} = \tau \phi S_g D_{12}^0 \frac{P_0}{P} \left(\frac{T + 273.15}{273.15} \right)^{\theta} \quad (3)$$

where the exponent θ is typically 1.8 (Pruess, 1987).

In the case of pure ordinary diffusion (no advection), the ADM reduces to

$$F_{i=1} = -D_{12} \rho_g \nabla \omega_{i=1} \quad (4a)$$

$$F_{i=2} = -D_{12} \rho_g \nabla \omega_{i=2} \quad (4b)$$

For a binary mixture, $\nabla \omega_{i=1} = -\nabla \omega_{i=2}$, so

$$F_{i=1} = -F_{i=2} \quad (5)$$

and the mass fluxes of the two components are equal and opposite.

DISCLAIMER

Dusty-Gas Model

The Dusty-Gas Model (DGM) was developed to describe gas transport through porous media including the coupling between the various transport mechanisms. The term dusty-gas is used because the porous medium consists of large "dust" molecules fixed in space that are treated as a component of the gas mixture. The kinetic theory of gases is applied to this dusty-gas mixture. The DGM, including numerous data-model comparisons, is discussed in detail by Mason and Malinauskas (1983) and by Cunningham and Williams (1980). The present discussion is limited to a binary gas mixture. In addition, temperature gradients and external forces such as gravity are ignored. The more complex nonisothermal and/or multicomponent system is treated in the DGM references given above.

Similar to the ADM, the DGM considers advection, Knudsen diffusion, and ordinary diffusion. One of the key aspects of the DGM is the combination of diffusion (ordinary and Knudsen) and advection. Ordinary and Knudsen diffusion are combined through addition of momentum transfer based on kinetic-theory arguments, and diffusive fluxes (ordinary plus Knudsen) are added to advective fluxes based on Chapman-Enskog kinetic theory.

There are many alternative forms of the DGM that can be derived by combining various forms of the equations. Thorstenson and Pollock (1989) present a number of useful forms for binary mixtures that are of special interest here. In particular, the total mole flux of component 1 in an isothermal binary system can be written as

ADM - DGM COMPARISON

The predictions for both models were made by the TOUGH2 code (Pruess, 1991). The code was modified to use the DGM gas transport expressions.

Comparison to Fundamental Relationships and Experimental Data

Two important relationships were discovered by Thomas Graham in the 1800's for gas diffusion in a binary mixture (Mason and Malinauskas, 1983). For Knudsen diffusion, or free-molecule flow, Graham's law of effusion applies as experimentally discovered by Graham (1846). Similarly, for ordinary diffusion without advection, the ratio of the diffusive fluxes is given by Graham's law of diffusion as experimentally discovered by Graham (1833). The ratio of diffusive mole fluxes for **both** regimes is the same, or

$$-J_{1K}/J_{2K} = -J_{1D}/J_{2D} = (m_2/m_1)^{1/2} \tag{8}$$

while the diffusive mass flux ratio is

$$-F_{1K}/F_{2K} = -F_{1D}/F_{2D} = (m_1/m_2)^{1/2} \tag{9}$$

The above relationships are very important. Graham's laws were misunderstood and were independently rediscovered in the 1950's and 1960's (Mason and Malinauskas, 1983). Graham's laws are fundamental relationships for gas diffusion and were used in the development of the DGM. The data of Evans, Watson, and Truitt (1962, 1963) strongly support Graham's laws and show that the assumption of equimolar counterdiffusion is not correct.

$$J_1 = -\frac{\left[D_{1K}D_{12}\frac{P_g}{RT}\nabla x_1 + D_{1K}(D_{12} + D_{2K})x_1\frac{\nabla P_g}{RT} \right]}{(D_{12} + x_1 D_{2K} + x_2 D_{1K})} - x_1\frac{k_0 P_g}{\mu_g}\frac{\nabla P_g}{RT} \tag{6}$$

and the total mole flux is given by

$$J = J_1 + J_2 = -\frac{\left[D_{12}(D_{2K} - D_{1K})\frac{P_g}{RT}\nabla x_1 - (D_{12}(x_1 D_{1K} + x_2 D_{2K}) + D_{1K}D_{2K})\frac{\nabla P_g}{RT} \right]}{(D_{12} + x_1 D_{2K} + x_2 D_{1K})} - \frac{k_0 P_g}{\mu_g}\frac{\nabla P_g}{RT} \tag{7}$$

In equation 6, the flux of component 1 consists of a diffusive flux (first term) and an advective flux (second term). The diffusive flux has ordinary diffusion (mole fraction gradient) and Knudsen diffusion (pressure gradient) components, similar to the ADM equation.

Evans, Watson, and Truitt Data

Evans, Watson, and Truitt (1962, 1963) performed a number of experiments for flow and diffusion of helium and argon across low-permeability graphite. Pure helium was present on one side, while pure argon was present on the other. These data were obtained to support the DGM as summarized by Mason and Malinauskas (1983).
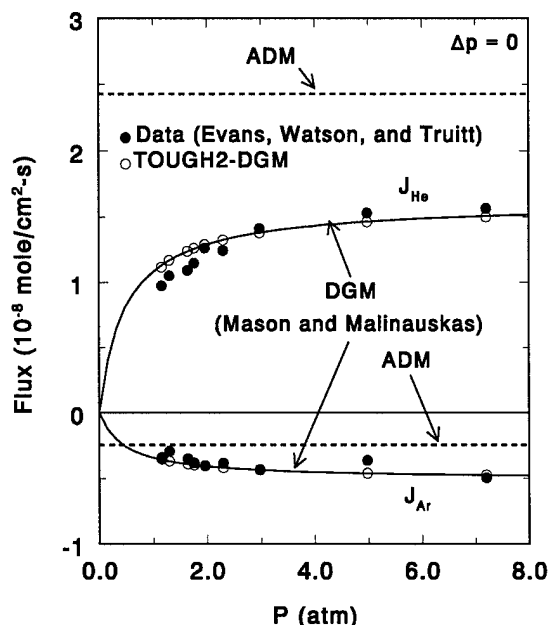
Figure 1
**Mole Flux Data-Model Comparison for Zero
Pressure Difference Conditions**

Zero Pressure Difference

The first data-model comparison considers zero pressure difference such that there is only diffusion. From Graham's laws, if only diffusion is occurring, the ratio of the mole fluxes (not the magnitude) for Knudsen diffusion and for ordinary diffusion is the same. Based on the molecular weights of helium (m=4.00) and argon (m=39.944), Graham's Laws give a mole flux ratio of helium to argon of 3.2.

Figure 1 compares the data with the predictions from the ADM and the DGM as a function of the average pressure. Helium mole flux is positive, while argon mole flux is negative. The mole flux data for both gases increase with increasing pressure. The DGM predicts the variation of the data quite well. The ratio of the mole fluxes is consistent with the theoretical ratio given above. In contrast, the ADM predicts a constant mole flux value independent of pressure that is inconsistent with the data. As discussed earlier, for pure diffusion, the mass fluxes of the two components are equal in the current implementation of the ADM. The ADM mole flux ratio (helium/argon) is simply the inverse of the ratio of the molecular weights, or about 10; this ratio is much higher than the data. The ADM overpredicts the helium mole flux and underpredicts the argon mole flux. The ADM, which in this case is simply Fick's law, does not predict the correct gas diffusion values or trends for this simple diffusion-only case.

The constant flux prediction for the ADM can be explained by analyzing the formulation. In the ADM, only ordinary diffusion is important for zero pressure difference conditions; Knudsen diffusion is not invoked through the Klinkenberg factor because there is no pressure difference and no advective flow. For the ADM, the mass flux due to ordinary diffusion was given earlier where the diffusion coefficient, D_{12}, is inversely proportional to pressure. The gas density increases with pressure while the diffusion coefficient decreases with pressure. Therefore, for pure diffusion of perfect gases, the ADM will predict a constant mass and mole flux as a function of pressure.

Zero Net Mole Flux

The second case simulates what would occur in a closed volume, where the total mole fluxes of the helium and argon components are equal, $J_{He} = -J_{Ar}$. In this situation, diffusion and advection balance each other resulting in a zero net mole flux. The predicted flux corresponding to this condition, and the pressure difference across the low-permeability graphite associated with it, are compared to the experimental data.

Figure 2 shows the predicted mole flux for the ADM and the DGM along with the data as a function of the average pressure. The DGM predictions compare reasonably well with the experimental data including the variation of flux with pressure. In contrast, the ADM predicts a constant mole flux as a function of pressure similar to the zero pressure difference case. The ADM predictions are about 20% to 50% too high depending on the pressure; the higher error is for the lower pressures.

Figure 3 presents the data for the pressure difference across the low-permeability graphite sample and the model predictions. The pressure difference is the value required for equal and opposite mole fluxes across the graphite. The data are well predicted by the DGM. The DGM predicts a maximum pressure difference at an average pressure of about 1 atmosphere; the data are not sufficient to resolve the details of this behavior. The shape of the DGM pressure difference curve is due to the dominance of Knudsen diffusion pressure drop at low pressures and the dominance of advection pressure drop at higher pressures. The ADM consistently overpredicts the pressure difference by a factor of 2 or more and does not have the predicted shape of the DGM.
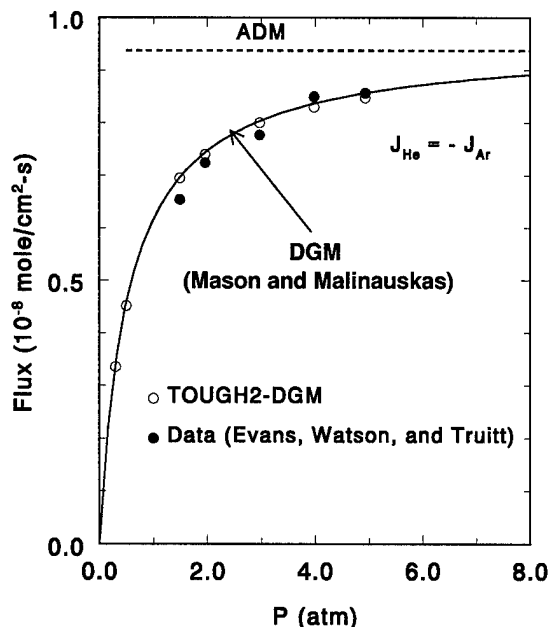
Figure 2
Mole Flux Data-Model Comparison
for Zero Net Mole Flux Conditions

Figure 3
Pressure Difference Data-Model Comparison
for Zero Net Mole Flux Conditions

Combined Advection and Diffusion

The next case is the most general situation of combined advection and diffusion. In this series of tests, the pressure difference across the test section was varied while maintaining the same average pressure. The individual fluxes of helium and argon across the low-permeability graphite test section were recorded at steady-state conditions. The predicted mole fluxes as a function of pressure difference are compared in Figures 4 and 5. Figure 4 presents the results for the ADM. The ADM predictions do not compare favorably with the data. Errors of a factor of 2 and greater are noted for the individual fluxes with corresponding differences in the net flux. While the general behavior is observed, the detailed variation is not reproduced by the ADM approach. In Figure 5, DGM predictions of the mole fluxes are shown. These results compare quite well with the data for the individual mole fluxes of helium and argon as well as with the net flux, including the variation with pressure difference.

Linear Air-Water Heat Pipe

On a practical basis, many multiphase advection-diffusion problems involve air and water vapor. For this combination of gases (assuming air is a single component), the molecular weight ratio is only about 1.6 compared to approximately 10 for the He-Ar system studied by Evans, Watson, and Truitt. In addition, the mole fraction differences for an air-water vapor system are considerably more limited for
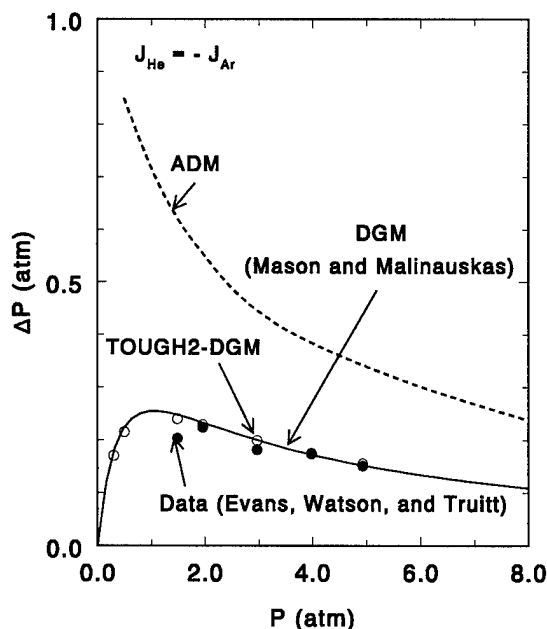
typical conditions. The problem chosen for comparison of the ADM and DGM for an air-water vapor system is a two-phase linear air-water porous media heat pipe. This problem was also selected because it was used for TOUGH code verification.

Figure 6 shows the thermodynamic results for the ADM and DGM. Note that the liquid saturation is scaled relative to the residual liquid saturation. The predictions from both models are very similar except for the liquid saturation near z=0, where the liquid saturation is higher for the DGM. Otherwise, the temperature, gas pressure, liquid saturation, and air mole fraction in the gas phase are practically the same. The linear heat pipe is driven by heat, and water evaporation/condensation is the dominant flow process. The total (advection plus diffusion) water vapor flow rates for the ADM and DGM are shown in Figure 7. Water vapor flows from the hot (right) end, where evaporation occurs, to the cold (left) end, where it condenses. The values for both models are practically identical due to the prescribed heat flux.

DISCUSSION

Two commonly used models for gas-phase diffusion and advection in porous media, the Advective-Dispersive Model (ADM) and the Dusty-Gas Model (DGM), have been compared. Evaluation of the models against Graham's laws and He-Ar data dramatizes the significant differences between the models. The DGM should, and does, agree very well with Graham's laws and the He-Ar
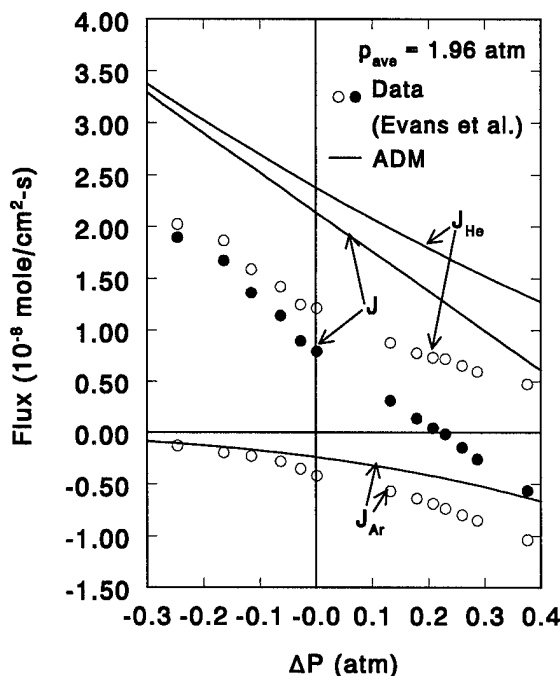
Figure 4
ADM Mole Flux Data-Model Comparison
For Combined Advection and Diffusion

Figure 5
DGM Mole Flux Data-Model Comparison
For Combined Advection and Diffusion

data because both were used in the model development and validation of the DGM. In contrast, the ADM does not agree well with either Graham's laws or the experimental data. The magnitude and the trend of the ADM predictions, such as the mole flux variation with pressure for pure diffusion, are significantly different than the data. In this case, the DGM is significantly better than the ADM, which may give incorrect trends and/or misleading results.

Model predictions for an air-water vapor system have also been compared. This system has similar molecular weights for the gas components, and the mole fraction difference is relatively small. The predicted difference between the two models is small in this case. Webb (1996, 1998) provides more details on the comparison on these two models, including parameter values and additional cases.

CONCLUSIONS

1. The ADM and DGM both consider advection, Knudsen diffusion, and ordinary diffusion. While the advective flow component can be shown to be the same for both models, significant differences may exist for the diffusion fluxes.

2. The DGM observes the fundamental relationships for diffusive fluxes given by Graham's laws. In contrast, the ADM violates these fundamental relationships.
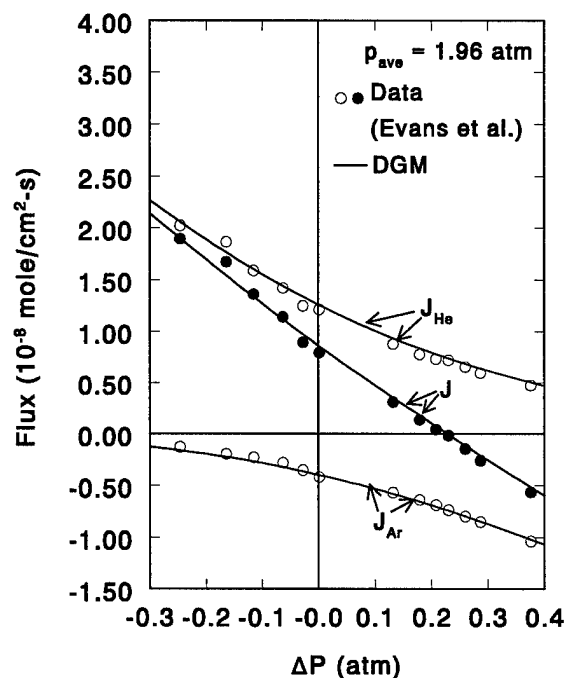
3. DGM predictions are in excellent agreement with the comprehensive experimental He-Ar data of Evans, Watson, and Truitt (1962, 1963). ADM predictions are in disagreement with the magnitude and some of the trends of the data.

4. The common conception of equimolar counterdiffusion is not supported by Graham's laws or by the He-Ar data of Evans, Watson, and Truitt (1962, 1963).

5. If diffusion is an important transport mechanism, the DGM is significantly better than the ADM, although the ADM may give reasonable qualitative results. For quantitative analysis and the analysis of diffusion trends, the DGM should be used because the ADM may give incorrect trends and/or misleading results.

NOMENCLATURE

b	Klinkenberg factor
D_{iK}	Knudsen diffusion coefficient for gas i
D_{12}	effective binary diffusion coefficient
D^0_{12}	free space binary diffusion coefficient at 1 bar and 0°C
F	mass flux
g_c	gravitational constant
J	mole flux
J_{iD}	ordinary diffusion mole flux
J_{iK}	Knudsen diffusion mole flux
k	permeability
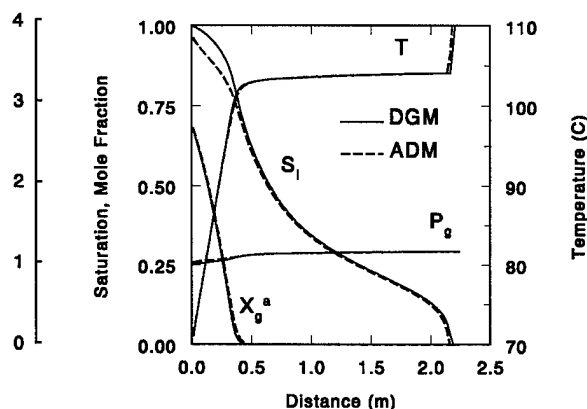
Figure 6
Linear Heat Pipe Thermodynamic Results

Figure 7
Linear Heat Pipe Vapor Flow Rates

P	pressure
P_0	pressure of 1 bar
R	universal gas constant
T	temperature
x	mole fraction

Greek symbols

μ	viscosity
ρ	density
τ	tortuosity
ϕ	porosity
ω	mass fraction
θ	exponent on diffusion coefficient

Subscripts

g	gas
r	relative
0	intrinsic
1,2	species or component number

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