GAS TRANSPORT IN POROUS MEDIA

Theory and Applications of Transport in Porous Media

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Gas Transport in Porous Media

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CHAPTER 1

INTRODUCTION

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Gas and vapor transport in porous media occur in a number of important applications including drying of industrial and food products, oil and gas exploration, environmental remediation of contaminated sites, and carbon sequestration. Understanding the fundamental mechanisms and processes of gas and vapor transport in porous media allows models to be used to evaluate and optimize the performance and design of these systems.

In this book, gas and vapor are distinguished by their available states at standard temperature and pressure (20°C, 101 kPa). If the gas-phase constituent can also exist as a liquid phase at standard temperature and pressure (e.g., water, ethanol, toluene, trichlorothylene), it is considered a vapor. If the gas-phase constituent is non-condensable at standard temperature and pressure (e.g., oxygen, carbon dioxide, helium, hydrogen, propane), it is considered a gas. The distinction is important because different processes affect the transport and behavior of gases and vapors in porous media. For example, mechanisms specific to vapors include vapor-pressure lowering and enhanced vapor diffusion, which are caused by the presence of a gas-phase constituent interacting with its liquid phase in an unsaturated porous media. In addition, the "heat-pipe" exploits isothermal latent heat exchange during evaporation and condensation to effectively transfer heat in designed and natural systems.

The intent of this book is to expose the reader to a variety of important studies of gas and vapor transport in porous and fractured media. The primary focus is on the presentation of fundamental processes, state-of-the-art modeling, experiments, and applications that are relevant to gas and vapor transport in porous and fractured media. The topics in this book span multiple disciplines, ranging from soil science to engineering. This has been done intentionally to integrate the broad audience in this subject area and to provide a compilation of common areas of research. Historically, the treatment of gas and vapor transport processes in porous and fractured media has been segregated according to disciplines or journals. Approaches to understanding these processes have evolved in soil science for many decades, but there has been

C. Ho and S. Webb (eds.), Gas Transport in Porous Media, 1–2.

relatively little cross-fertilization of these studies and findings into other disciplines such as engineering. Some processes such as enhanced vapor diffusion have been investigated by researchers in soil sciences as far back as the 1950s and 1960s, but they are only recently being considered in engineering applications such as drying of porous materials.

Another motivation for this book is to identify applications where gas and vapor transport are important or dominant mechanisms. Often, the importance of gas and vapor transport mechanisms is overlooked or overshadowed by studies of liquid-flow processes. However, advances in numerical modeling and experimental methods have allowed the simulation of coupled gas- and liquid-flow processes in complex media, and we are now able to distinguish the relative importance of mechanisms in various applications. Examples of recent applications in which gas and vapor transport processes are significant include nuclear waste disposal in geologic media and detection of unexploded ordnance in the subsurface.

This book is divided into three parts: Part 1 – Processes and Models; Part 2 – Measurement and Monitoring; and Part 3 – Applications. The first part, Processes and Models, presents fundamental processes associated with gas and vapor transport in porous media. Beginning with gas transport mechanisms, it describes advection and diffusion processes, including the Dusty-Gas Model. Vapor transport processes are then described in a similar manner, illustrating important features of a condensable gas in porous media such as enhanced vapor diffusion and vapor-pressure lowering. Vapor-solid sorption is also discussed because of its importance to recent applications in land-mine detection, and mechanisms involving evaporation and coupled processes are presented. The impact of heterogeneities and scaling on gas and vapor transport processing in porous and fractured media is also discussed. Two-phase processes and characteristics are also described, and various models of gas and vapor transport processes using continuum and Lattice Boltzmann models are presented.

In Part 2, Measurement and Monitoring, various methods are described that have been used to measure gas and vapor transport processes and parameters at the laboratory and field scales. Measurement of the diffusion coefficient, permeability, flow rate, constituent concentration, and mass flux of gas and vapors are described. New technologies and microelectronic sensors that measure gas-phase volatile organic compounds are also introduced.

Finally, in Part 3, Applications of gas and vapor transport in porous and fractured media are presented. Applications include radon transport, landmine detection, environmental remediation, geologic waste disposal, oil and gas exploration, carbon sequestration, and industrial processes.

This book provides a broad and interdisciplinary view of the different processes, models, experimental methods, and applications associated with gas and vapor transport in porous media. We hope that the reader develops an understanding of the many diverse topics and an appreciation for the important applications covered in this book.

PART 1

PROCESSES AND MODELS

CHAPTER 2

GAS TRANSPORT MECHANISMS

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Gas-phase momentum transport in porous media consists of advective and diffusive components. In this chapter, the individual advective and diffusive components will be presented separately first, followed by a discussion of the combined mechanisms. Gas-only situations will be discussed for all the mechanisms. Two-phase, or unsaturated, flow effects are included in Chapter 5.

The conservation equations presented below are given in a simplified form. For a complete derivation of the various conservation equations, including underlying assumptions, see Whitaker (Chapter 6 of this book).

Energy transport is not discussed in this chapter. Gas-phase energy transport in porous media is treated by Plumb (Chapter 27 of this book). Energy transport is also discussed in Nield and Bejan (1999) and Kaviany (1995).

2.1 GAS-PHASE ADVECTION

2.1.1 Darcy's Law

Gas-phase advection in porous media is generally analyzed using Darcy's law (Darcy, 1856), which simply states that the gas Darcy velocity, u_g, is directly proportional to the gas-phase pressure gradient, ∇P_g, and the gas-phase permeability, k_g. Darcy's law can be written as

$$\overline{u}_g = -\frac{k_g}{\mu_g}\left(\nabla P_g - \rho_g \overline{g}\right)$$

where μ_g is the gas-phase viscosity and $\overline{g}$ is the gravitational constant. In terms of mass flux, the equation is

$$\overline{F}_g = \rho_g \overline{u}_g = -\frac{k_g}{\mu_g}\rho_g\left(\nabla P_g - \rho_g \overline{g}\right)$$

C. Ho and S. Webb (eds.), Gas Transport in Porous Media, 5–26.

Neglecting gravity and rearranging

$$\nabla P_g = -\frac{\mu_g}{k_g}\,\overline{u}_g$$

Note that the Darcy velocity, u_g, is not a physical velocity. Rather, it is a superficial velocity based on the entire cross section of the flow, not just the fluid flow cross-section. The Darcy velocity is related to the pore velocity, V_g, through the porosity, ϕ, or

$$V_g = \frac{u_g}{\phi}$$

The gas-phase permeability, k_g, is a proportionality constant that is usually experimentally determined with units of length^2. The gas-phase permeability may be slightly different than the liquid-phase permeability due to the effects of the fluids. Values of the liquid-phase permeability vary widely, from 10^{-7} to 10^{-9} m^2 for clean gravel down to 10^{-18} to 10^{-20} m^2 for granite (Bear, 1979, pg. 68). The unit Darcy is often used, which is equal to 0.987×10^{-12} m^2.

Darcy's law is applicable to low velocity flow, which is generally the case in porous media flow, and to regions without boundary shear flow, such as away from walls. When wall shear is important, the Brinkman extension can be used as discussed below. For turbulent flow conditions, the Forchheimer equation is appropriate. In some situations (e.g., Vafai and Tien, 1981), the Brinkman and Forchheimer equations are both employed for a more complete momentum equation. For a more detailed discussion of the various flow laws, see Nield and Bejan (1999), Kaviany (1995), or Lage (1998).

2.1.2 Brinkman Extension

The Brinkman extension to Darcy's law equation includes the effect of wall or boundary shear on the flow velocity, or

$$\nabla P_g = -\frac{\mu_g}{k_g}\,\overline{u}_g + \tilde{\mu}\,\nabla^2 \overline{u}_g$$

where gravity has been ignored for clarity. The first term on the RHS is immediately recognizable as the Darcy expression, while the second term is a shear stress term such as would be required by a boundary wall no-slip condition. The coefficient $\tilde{\mu}$ is an effective viscosity at the wall, which in general is not equal to the gas viscosity, μ_g, as discussed by Nield and Bejan (1999). For many situations, the use of the boundary shear term is not necessary. The effect is only significant in a region close to the boundary whose thickness is of order of the square root of the gas permeability, $k_g^{1/2}$ (assuming $\tilde{\mu} = \mu_g$), so for most applications, the effect can be ignored.

The Brinkman equation is also often employed at the interface between a porous media and a clear fluid, or a fluid with no porous media, in order to obtain continuity of shear stress. This interfacial condition is discussed in more detail by Nield and Bejan (1999) and Kaviany (1995).

2.1.3 Forchheimer Extension

At low pore velocities, Darcy's law works quite well. However, as the pore velocities increase, the flow becomes turbulent, the flow resistance becomes non-linear, and the Forchheimer equation is more appropriate. From Joseph et al. (1982), the Forchheimer equation is

$$\nabla P_{\mathrm{g}} = -\,\frac{\mu_{\mathrm{g}}}{k_{\mathrm{g}}}\,\overline{u}_{\mathrm{g}} - c_{\mathrm{F}}\,k_{\mathrm{g}}^{-1/2}\,\rho_{\mathrm{g}}\left|\overline{u}_{\mathrm{g}}\right|\overline{u}_{\mathrm{g}}$$

where c_{F} is a constant and gravity has been ignored. The first term on the RHS is again immediately recognizable as Darcy's law. The second term on the RHS is a non-linear flow resistance term. According to Nield and Bejan (1999), the above equation is based on the work of Dupuit (1863) and Forchheimer (1901) as modified by Ward (1964). The value of c_{F} is approximately 0.55 based on the work of Ward (1964). However, later work indicates that c_{F} is a function of the porous medium and can be as low as 0.1 for foam metal fibers as summarized by Nield and Bejan (1999). In addition, Beavers et al. (1973) showed that bounding walls can change the value of c_{F} significantly.

The above equation can be rearranged in terms of a permeability-based Reynolds number, where the characteristic dimension is the square root of the gas permeability, or

$$\mathrm{Re}_k = \frac{\rho_{\mathrm{g}}\,u_{\mathrm{g}}\,k_{\mathrm{g}}^{1/2}}{\mu_{\mathrm{g}}}$$

The Forchheimer equation can be rearranged in terms of the value of c_{F} and the Reynolds number, or

$$\nabla P_{\mathrm{g}} \propto \left[\frac{1}{\mathrm{Re}_k} + c_{\mathrm{F}}\right]$$

According to Nield and Bejan (1999), the transition from Darcy's law ($c_{\mathrm{F}} = 0.$) to the above Forchheimer equation occurs in the permeability-based Reynolds number range of 1 to 10. Note that this transition is based on liquid flow through an isothermal liquid-saturated porous medium, not an all-gas system. At low Reynolds numbers, Darcy's law is recovered ($c_{\mathrm{F}} \ll 1/\mathrm{Re}_k$). As the Reynolds number increases, the pressure drop increases above that predicted by Darcy's law. For further details, see the discussion in Nield and Bejan (1999).

More recently, porous media approaches have been developed that include a two-equation turbulence model similar to that used in clear fluid computational fluid dynamics codes as exemplified by Masuoka and Takatsu (1996), Antohe and Lage (1997), and Getachew et al. (2000).

2.1.4 Low Permeability Effects

Gas advection through porous media can be idealized as flow through numerous capillary tubes. For large capillary tubes, the gas molecular mean free path is much smaller than the radius, and continuum flow occurs. As the capillary tubes get smaller and smaller, the gas molecular mean free path becomes of the same order, and free-molecule, or Knudsen, diffusion becomes important.

Low permeability effects were experimentally investigated by Knudsen in 1909 for gas flow in capillaries as discussed by Cunningham and Williams (1980, pg. 49). Based on Darcy's law, the mass flux for a given pressure drop should decrease as the average pressure is reduced due to the change in gas density. However, Knudsen found that at low pressures, the mass flux reaches a minimum value and then increases with decreasing pressure, which is due to slip, or the fact that the fluid velocity at the wall is not zero due to free-molecule flow.

Klinkenberg (1941) derived an expression for the effective gas permeability, k_g, of a single gas in the Knudsen diffusion regime, which is a function of the liquid permeability, k_λ, the average pressure, $\overline{P}$, and the Klinkenberg coefficient of gas i, b_i, or

$$k_{\mathrm{g,i}} = k_\ell \left(1 + \frac{b_i}{\overline{P}_\mathrm{g}}\right)$$

For a large average pressure, the correction factor in parentheses goes to zero, and the gas and liquid permeabilities tend to become equal. As the average pressure decreases, the two permeabilities can deviate significantly from each other. This behavior is confirmed by data presented by Klinkenberg (1941) for glass filters and core samples and by Reda (1987) for tuff. The Klinkenberg parameter for a given porous medium can be derived by plotting the effective gas permeability as a function of the inverse of the average pressure. The slope of the line is related to the Klinkenberg parameter, and the intercept at zero inverse average pressure is the liquid permeability.

The Klinkenberg coefficient, b_i, is a function of the porous medium, the gas, and the temperature. The Klinkenberg coefficient for air can be estimated from the Heid et al. (1950) correlation for air at 25°C as a function of permeability (Thorstenson and Pollock, 1989a, Figure 3), or

$$b_\mathrm{air} = 0.11\, k_\ell^{-0.39}$$

where b_air is in Pa and k_ℓ is the liquid permeability in m^2. The data used in this correlation are from oil-field cores with permeability values between about 10^{-12} and 10^{-17} m^2.

Another expression for the Klinkenberg coefficient is from Jones and Owens (1980), who performed similar measurements for low-permeability gas sands with permeabilities between 10^{-14} and 10^{-19} m^2. They developed the following correlation for air (presumably at 25°C)

$$b_\mathrm{air} = 0.98\, k_\ell^{-0.33}$$

where the units are the same as for the Heid et al. (1950) correlation. Between 10^{-14} and 10^{-17} m^2, which is where the permeabilities for the data sets overlap, the Klinkenberg factors from both correlations are quite similar.

As discussed later on in Section 2.2.2, the Klinkenberg coefficient for a given porous media is different for each gas and is dependent on the local temperature. The Klinkenberg factor can be corrected for different conditions as follows

$$b_i = b_{\mathrm{ref}} \left(\frac{\mu_i}{\mu_{\mathrm{ref}}\,(T_{\mathrm{ref}})} \right) \left(\frac{m_{\mathrm{ref}}}{m_i} \right)^{1/2} \left(\frac{T_i}{T_{\mathrm{ref}}} \right)^{1/2}$$

where ref refers to the reference gas, which is usually air, and m is the molecular weight. The temperature is in absolute units.

As the permeability of the medium gets even lower, the pore dimensions approach those of a single molecule. At this point, the flow mechanisms change, and configurational diffusion (Cunningham and Williams, 1980) becomes important. As discussed in Section 2.2.2, the transition from Knudsen diffusion (Klinkenberg effect) to configurational diffusion is estimated to be at a permeability of approximately 10^{-21} m^2.

2.2 GAS-PHASE DIFFUSION

Diffusion in porous media consists of continuum, or ordinary, diffusion and free-molecule diffusion. Continuum diffusion refers to the relative motion of different gas species. Free-molecule diffusion, or Knudsen diffusion, refers to an individual gas and occurs when the mean-free path of the gas molecules is of the same order as the pore diameter of the porous media. As the pore size decreases further, configurational diffusion is encountered where the gas molecule size is comparable to the pore diameter. Configurational diffusion is briefly discussed in the free-molecule diffusion section.

A number of different models have been used to quantify gas diffusion processes in porous media, some of which will be discussed in the next section. Many of the models are simply models derived for a clear fluid (no porous media) that were simply adapted for a porous media. The clear fluid diffusion models only consider molecular diffusion and do not include Knudsen diffusion. Other models are specifically derived for porous media applications. Molecular diffusion and Knudsen diffusion are included in their formulation.

2.2.1 Ordinary (Continuum) Diffusion

Fick's law is the most popular approach to calculating gas diffusion in clear fluids (no porous media) due to its simplicity. While it is only strictly applicable to clear fluids, it has been extensively applied to porous media situations through introduction of a porous media factor. Another approach often employed is the Stefan-Maxwell equations. This equation set is simply an extension to Fick's law for a multicomponent mixture as discussed by Bird, Stewart, and Lightfoot (1960, pg. 569) (hereafter BSL). While attempts have been made to define effective diffusion parameters to account for the presence of the porous medium, the basic transport equations are not altered.

2.2.1.1 Fick's law

Fick's law is actually two laws. Fick's first law is the relationship of the diffusive flux of a gas component as a function of the concentration gradient under steady-state conditions. Fick's second law relates the unsteady diffusive flux to the concentration gradient. Both laws were originally derived for clear fluids (no porous media).

First Law

Clear Fluids

Fick's first law for a binary system basically states that the mole or mass flux is proportional to a diffusion coefficient times the gradient of the mole or mass concentration. For the mole flux formulation, Fick's first law of diffusion for the mole flux of component A, $J_{\mathrm{A}}^{\mathrm{M}}$, in one dimension in a clear fluid (no porous medium) is

$$J_{\mathrm{A}}^{\mathrm{M}} = -c\, D_{\mathrm{AB,CF}}\, \nabla x_{\mathrm{A}}$$

where c is the concentration of the gas, $D_{\mathrm{AB,CF}}$ is the diffusion coefficient in a clear fluid, and x_{A} is the mole fraction of component A. The above form of Fick's first law is commonly misused. The M superscript on the mole flux denotes that the mole flux is relative to the molar-average velocity, NOT to stationary coordinates (BSL, pg. 502). The mole flux equation relative to stationary coordinates for a binary system is given by

$$N_{\mathrm{A}}^{\mathrm{D}} - x_{\mathrm{A}} \left(N_{\mathrm{A}}^{\mathrm{D}} + N_{\mathrm{B}}^{\mathrm{D}} \right) = -c\, D_{\mathrm{AB,CF}}\, \nabla x_{\mathrm{A}}$$

where N is relative to stationary coordinates. The second term on the LHS is the molar-average velocity. The mass flux form relative to stationary coordinates is

$$F_{\mathrm{A}} - \omega_{\mathrm{A}}\, (F_{\mathrm{A}} + F_{\mathrm{B}}) = -\rho_{\mathrm{g}}\, D_{\mathrm{AB,CF}}\, \nabla \omega_{\mathrm{A}}$$

where F is the mass flux and ω_{A} is the mass fraction of component A.

Fick's first law and a number of equivalent forms (mole and mass forms, relative to mole or mass velocities or stationary coordinates) are discussed in great detail by BSL (Chapter 16). The relationships between the various fluxes are also discussed in detail in BSL (Chapter 16). However, many applications that use Fick's first law overlook the coordinate system issues. In particular, many applications use Fick's law for the molar-average velocity and incorrectly apply it to stationary coordinates as discussed later in this chapter.

Porous Media

The above forms of Fick's law are appropriate for clear fluids. For application to porous media, Fick's first law is often modified by the introduction of a porous media factor, β, or

$$D_{\mathrm{AB}}^{*} = \beta\, D_{\mathrm{AB,CF}}$$

The term β is defined as

$$\beta = \phi\, S_g\, \tau$$

where D^*_{AB} is the effective diffusion coefficient for the AB gas system in a porous media, $D_{AB,CF}$ is the effective diffusion coefficient of the AB gas system in a clear fluid, ϕ is the porosity, S_g is the gas saturation (equal to 1.0 for all-gas conditions), and τ is the tortuosity. The tortuosity factor is discussed in further detail below.

Similar to the clear fluid equation, the mole flux through a porous media relative to stationary coordinates is given by

$$\begin{aligned} F_A - \omega_A\ (F_A + F_B) &= -\beta\, \rho_g\, D_{AB,CF}\, \nabla\omega_A \\ &= -\rho_g D^*_{AB} \nabla\omega_A \end{aligned}$$

Inclusion of the β term takes into account the effective area for gas flow in the pores ($\phi\, S_g$) and the porous media tortuosity (τ). The diffusion coefficient $D_{AB,CF}$ can be estimated from correlations as discussed by Reid et al. (1987). The diffusion coefficient for gases is inversely proportional to the absolute pressure and directly proportional to the absolute temperature to the 1.75 power as given by the Fuller et al. correlation discussed in Reid et al. (1987).

The tortuosity factor, τ, as defined in this application as the ratio of the length of the "tortuous" path in a porous media divided by a straight line value. The tortuosity factor is evaluated for diffusion, not advection. For clear fluids, the tortuosity is equal to 1.0. Note that sometimes other definitions of the tortuosity factor are used (Dullien, 1992, pg. 311). There are a number of models for the tortuosity factor. The most widely used correlation is that of Millington and Quirk (1961). The tortuosity correlation of Millington and Quirk (1961) is given by

$$\tau = \phi^{1/3} S_g^{7/3}$$

which can be rewritten as

$$\tau = \tau_o\, \tau_{S_g} = \phi^{1/3} S_g^{7/3}$$

where τ_o is the tortuosity due to the structure of the porous medium and τ_{S_g} is the tortuosity due to the partial saturation. For all-gas conditions as discussed in this chapter, the tortuosity factor reduces to the porous medium value, or

$$\tau\ (S_g = 1.0) = \tau_o = \phi^{1/3}$$

Costanza-Robinson and Brusseau (Chapter 7 of this book) discuss porous media tortuosity.

Second Law

Fick's second law of diffusion for clear fluids is concerned with the temporal evolution of the concentration, or (BSL, pg. 558)

$$\frac{\partial c_{\mathrm{A}}}{\partial t} = D_{\mathrm{AB}}\, \nabla^2 c_{\mathrm{A}}$$

which is only strictly applicable if the molar-average velocity is zero, or for equimolar counterdiffusion. This equation is similar to the heat conduction equation, so many solutions exist such as in Carslaw and Jaeger (1959).

The rest of the present chapter is concerned with Fick's first law, not Fick's second law. For an excellent discussion of Fick's second law, see Fen and Abriola (2004). Abriola et al. (1992) and Sleep (1998) also evaluate Fick's second law.

2.2.1.2 Stefan-Maxwell Equations

Fick's first law of diffusion presented above is applicable to binary gases. This restriction is due to the fact that the gradients of the two gases are directly related to each other, so only a single gradient needs to be specified. For multicomponent gases, multiple gradients need to be determined. For an ideal mixture, the component mass flux equations can be manipulated resulting in (BSL, pg. 569)

$$\nabla x_i = \sum_{j=1}^{n} \frac{1}{c\,D_{ij}} \left(x_i\, N_j \; - \; x_j\, N_i \right)$$

which are known as the Stefan-Maxwell equations applicable to stationary coordinates in a clear fluid. For a two-component system, the Stefan-Maxwell equations reduce to Fick's first law. For application to a porous medium, the diffusion coefficients need to be modified as discussed above.

2.2.2 Free-Molecule Diffusion

As discussed earlier, when the gas molecular mean free path becomes of the same order as the tube dimensions, free-molecule, or Knudsen, diffusion becomes important. Due to the influence of walls, Knudsen diffusion and configurational diffusion implicitly include the effect of the porous medium. Unlike ordinary (continuum) diffusion, there are no approaches for the free-molecule diffusion regime that use clear fluid approaches modified to include porous media effects.

The molecular flux of gas i due to Knudsen diffusion is given by the general diffusion equation (Mason and Malinauskas, 1983, pg. 16)

$$J_{i\mathrm{K}} = -D_{i\mathrm{K}}\, \nabla n_i$$

where n_i is the molecular density and $D_{i\mathrm{K}}$ is the Knudsen diffusion coefficient. The Knudsen diffusivity of gas i for a capillary of a given radius can be estimated as follows (Cunningham and Williams, 1980, eqns. 2.17 and 2.65) assuming a coefficient of diffuse reflection equal to unity

$$D_{i\mathrm{K,capillary}} = \frac{2}{3}\left(\frac{8RT}{\pi m_i}\right)^{1/2} r_{\mathrm{capillary}}$$

This equation can be written as

$$D_{i\mathrm{K,capillary}} = 97.0\left(\frac{T}{m_i}\right)^{1/2} r_{\mathrm{capillary}}$$

where $D_{i\mathrm{K,capillary}}$ is in m^2/s, T is in K, m is the molecular weight, and $r_{\mathrm{capillary}}$ is in m. While this equation may be appropriate for flow in well-defined capillaries, it is not directly useful for porous media applications. However, there is an alternative way to determine the Knudsen diffusion coefficient that includes the complexity of the porous media.

The equation for the molecular flux from Knudsen diffusion can be rewritten in the same form as Darcy's law. From this expression, and Klinkenberg's formula, the Knudsen diffusion coefficient, $D_{i\mathrm{K}}$, can be related to the Klinkenberg factor as follows (Thorstenson and Pollock, 1989a, eqn 60)

$$D_{i\mathrm{K}} = \frac{k_{\mathrm{g}}\, b_i}{\mu_i}$$

As discussed in the advection part of this chapter, there are a number of correlations for the Klinkenberg coefficient, b_i, as a function of the porous medium, the fluid, and the temperature. The Klinkenberg coefficient can be used in the above equation to evaluate the Knudsen diffusion coefficient for a porous medium. The Klinkenberg coefficient implicitly takes into account the structure of the porous medium as reflected through the permeability. The modifications to the Klinkenberg factor due to the gas (molecular weight and viscosity) and the temperature should be used as discussed earlier in Section 2.1.4.

As the permeability of the medium gets even lower, the pore dimensions approach those of a single molecule. At this point, the flow mechanisms change, and configurational diffusion (Cunningham and Williams, 1980) becomes important. In configurational diffusion, the size of the molecules is comparable to the pore dimensions, and the molecular configuration becomes important (e.g., Xiao and Wei, 1992a, b). Membrane diffusion occurs at even smaller pore sizes where the chemical characteristics of the molecules are important (Cunningham and Williams, 1980).

Cunningham and Williams (1980) suggest that configurational diffusion may be encountered when the pore sizes are less than about 10 Å. Note that the molecular size can be characterized by the Lennard-Jones length constant, σ, which varies from about 2.5 to 7.5 Å as given by BSL (1960, pg. 744). Assuming a porosity of about 10%, and calculating the tortuosity by the Millinton and Quirk relationship given earlier, the effective Knudsen diffusion coefficient will be about 10^{-9} m^2/s. Using the Jones and Owens (1980) correlation for the Klinkenberg coefficient, the permeability is about 10^{-21} m^2. This prediction of the transition from Knudsen diffusion to configuration diffusion is qualitative at best. However, it should indicate the approximate permeability where configurational diffusion should at least be considered to be as the possible diffusion mechanism.

2.3 COMBINED MECHANISMS

The interaction between advection and diffusion in porous media can be significant. Consider two separate volumes connected by a tube containing a light gas and a heavy gas. Diffusion of the light gas is faster than the heavy gas because of the higher molecule velocity. The net flow of molecules is toward the heavy gas volume, so the pressure rises in the heavy gas volume and decreases in the light gas volume. In turn, this pressure difference causes advection from the heavy gas volume to the light gas volume. Thus, diffusion directly leads to advection. Only in the case of equimolar gases will diffusion not result in advection.

As mentioned earlier, this scenario was implicitly included in the diffusion formulation discussed by BSL in that diffusion is relative to the molar-average velocity. However, this effect has generally been ignored. Coupling of the advection and diffusion mechanisms has been formalized with the development of the Dusty Gas Model by Evans, Mason and colleagues (Evans et al., 1961; Evans et al., 1962a; Mason et al., 1963; Mason et al., 1964). The Dusty Gas Model (DGM) takes the gas transport equations a step further by including the effect of the porous media as a “dusty gas” component of the gas mixture. The “dusty gas” is assumed to consist of large molecules fixed in space that is treated as a component of the gas mixture. The kinetic theory of gases is applied to this dusty-gas mixture. 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.

The DGM, including numerous data-model comparisons, is discussed in detail by Mason and Malinauskas (1983) and by Cunningham and Williams (1980). Other excellent references on application of the Dusty Gas Model for porous media are Thorstenson and Pollock (1989a, 1989b) and Jackson (1977).

The exclusive presentation of the DGM in this chapter does not imply that the DGM is the most comprehensive gas-phase diffusion model available for porous media. There are a number of other models available including Feng and Stewart (1973), who extended the DGM to more complicated pore networks, a mean transport pore model as presented by Arnost and Schneider (1995) (see Šolcová and Schneider (Chapter 14 of this book)), and Shapiro (1993), who developed a model for heterogeneous anisotropic porous media. Altevogt et al. (2003a, b) present an alternate approach for binary gas diffusion. Rather, the DGM is the most widely used model for a mechanistic approach to combine gas advection and diffusion in porous media at the present time.

Ignoring thermal diffusion, which is typically small, the DGM can be written either in terms of the diffusive molar flux, N^{D}, or the total molar flux (diffusive plus advective), N^{T}, which are relative to fixed coordinates (Thorstenson and Pollock, 1989a, eqns. 41 and 48). The two expressions are

$$\sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_i N_j^{\mathrm{D}} - x_j N_i^{\mathrm{D}}}{D_{ij}^{*}} - \frac{N_i^{\mathrm{D}}}{D_{i\mathrm{K}}} = \frac{\nabla P_i}{RT} = \frac{P\nabla x_i}{RT} + \frac{x_i \nabla P}{RT}$$

$$\sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_i N_j^{\mathrm{T}} - x_j N_i^{\mathrm{T}}}{D_{ij}^{*}} - \frac{N_i^{\mathrm{T}}}{D_{i\mathrm{K}}} = \frac{P\nabla x_i}{RT} + \left(1 + \frac{k_\ell P}{D_{ik}\mu}\right)\frac{x_i \nabla P}{RT}$$

where the second equation simply includes the advective flux on both sides of the equation. The first term on the LHS considers molecule-molecule interactions and is immediately recognized as being based on the Stefan–Maxwell equations discussed earlier. The second term on the LHS considers molecule-particle (Knudsen diffusion) interactions, while the RHS is the driving force for diffusion and advection, which includes concentration and pressure gradients.

There are many forms of the DGM. One particularly useful form is for the total mass flux of component 1 in an isothermal binary system, or (Thorstenson and Pollock, 1989a, eqn. F4)

$$\begin{aligned} F_1 &= m_1 N_1^{\mathrm{T}} \\ &= -m_1 \frac{\left[D_{1\mathrm{K}} D_{12}^{*}(P/RT)\nabla x_1 + D_{1\mathrm{K}}(D_{12}^{*} + D_{2\mathrm{K}})x_1(\nabla P/RT)\right]}{(D_{12}^{*} + x_1 D_{2\mathrm{K}} + x_2 D_{1\mathrm{K}})} \\ &\quad - x_1 m_1 \frac{k_0 P}{\mu}\frac{\nabla P}{RT} \end{aligned}$$

The flux of component 1 has diffusive (first term) and advective (second term) components. The diffusive flux consists of ordinary diffusion (mole fraction gradient) and Knudsen diffusion (pressure gradient) components.

Note that in the special case of isobaric conditions ($\nabla P = 0$), the advective and Knudsen diffusion fluxes are zero. However, this does *not* mean that the Knudsen diffusion coefficients are not important. The ordinary diffusion flux is dependent on *both* diffusion (Knudsen and ordinary) coefficients. The Knudsen diffusion coefficients characterize the impact of the porous media (gas-wall interactions) on ordinary diffusion. This behavior is absent in the clear fluid formulations, such as Fick's law, that are modified for porous media applications.

2.4 COMPARISON TO FUNDAMENTAL RELATIONSHIPS AND EXPERIMENTAL DATA

In the 1800s, Thomas Graham discovered two important relationships for gas diffusion in a porous media that relate the diffusive fluxes of a binary mixture in a porous medium (Mason and Malinauskas, 1983, pg. 3). Graham's law of effusion applies to

Knudsen diffusion as experimentally discovered by Graham (1846), or

$$-\frac{N_1^{\mathrm{K}}}{N_2^{\mathrm{K}}} = \left(\frac{m_2}{m_1}\right)^{1/2}$$

For ordinary diffusion (no advection), Graham's law of diffusion applies as experimentally discovered by Graham (1833) or

$$-\frac{N_1^{\mathrm{D}}}{N_2^{\mathrm{D}}} = \left(\frac{m_2}{m_1}\right)^{1/2}$$

Even though the ratios are identical, each equation applies to a different diffusion regime. In terms of a mass flux ratio, these equations become

$$-\frac{F_1^{\mathrm{K}}}{F_2^{\mathrm{K}}} = \left(\frac{m_1}{m_2}\right)^{1/2}$$

$$-\frac{F_1^{\mathrm{D}}}{F_2^{\mathrm{D}}} = \left(\frac{m_1}{m_2}\right)^{1/2}$$

The above relationships are significant. Graham's laws were "lost" and were independently rediscovered in the 1950s and 1960s (Mason and Malinauskas (1983, pg. 3)). Graham's laws are fundamental relationships for gas diffusion in porous media and were used in the development of the Dusty Gas Model. These relationships will be used in the data-model comparisons that follow.

The data used in these comparisons were obtained by Evans, Watson, and Truitt (1962b, 1963). They performed these experiments to support development of the Dusty Gas Model. The experiments consisted of flow and diffusion of helium and argon across a low-porosity (0.11) and low-permeability (2.13×10^{-18} m^2) graphite. At this low permeability, Knudsen diffusion plays a significant role.

In addition to the data and model predictions, Mason and Malinauskas (1983, pg. 91) provide closed-form solutions for the DGM for special cases, which are also plotted as a continuous line labeled DGM in Figure 2.1 and Figure 2.2. In the data-model comparisons, the DGM is compared to the data as is a model labeled ADM. The ADM Model, which stands for advective-diffusive (or dispersive) model, is simply a linear addition of Darcy's law and ordinary diffusion using Fick's law, which is incorrectly applied to stationary coordinates as discussed above. This simple linear addition is commonly used as exemplified by TOUGH2 (Pruess, 1991) and Abriola and Pinder (1985). Slip effects, or Knudsen diffusion, are included through a Klinkenberg parameter to define an effective permeability for the advective flux as discussed earlier. 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 coupling between advective and diffusive mechanisms. The expression for the ADM used in this comparison is

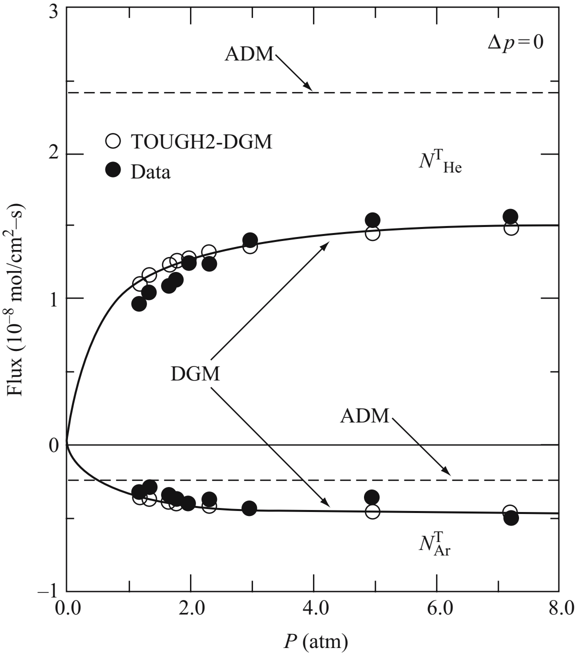
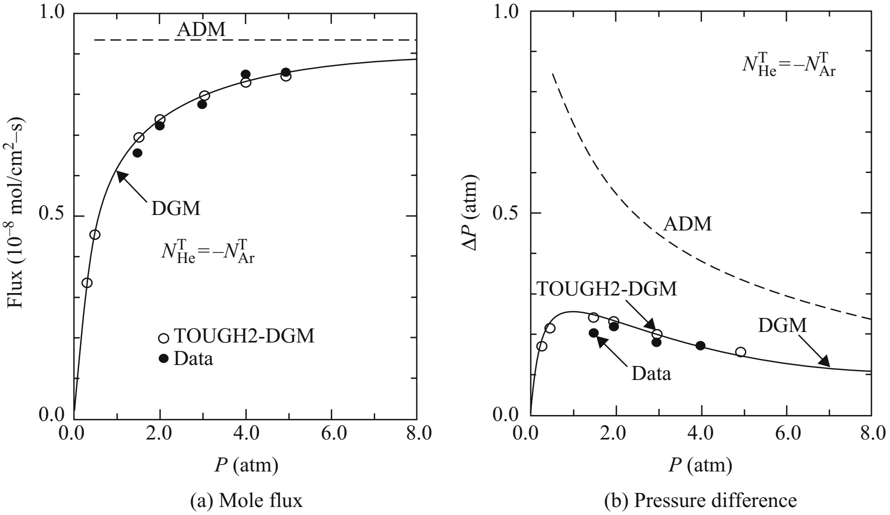


Figure 2.1. Mole flux data-model comparison for zero pressure difference conditions (reprinted from Webb, 1998 with permission with minor modifications)



(a) Mole flux (b) Pressure difference

Figure 2.2. Data-model comparison for zero net mole flux conditions (reprinted from Webb, 1998 with permission with minor modifications)

given below

$$F_g = -\frac{k_\ell}{\mu_g}\left(1 + \frac{b_g}{P_g}\right)\rho_g\,(\nabla P_g - \rho_g \overline{g}) - \rho_g D_{12}^* \nabla x$$

The DGM and the ADM results presented in this section were calculated by the TOUGH2 code (Pruess, 1991), which was modified to incorporate the DGM by Webb (1998). Pruess (Chapter 12 of this book) summarizes the flux expressions in many commonly used porous media codes including TOUGH2.

2.4.1 Zero Pressure Difference

The first data-model comparison considers zero pressure difference across the porous media. In this case, there is diffusion but no advection. From Graham's laws, the ratio of the mole fluxes (not the magnitude) for Knudsen diffusion and for ordinary diffusion is the same. Graham's laws give a mole flux ratio of helium to argon of 3.2 based on the molecular weights of helium ($m = 4.00$) and argon ($m = 39.944$).

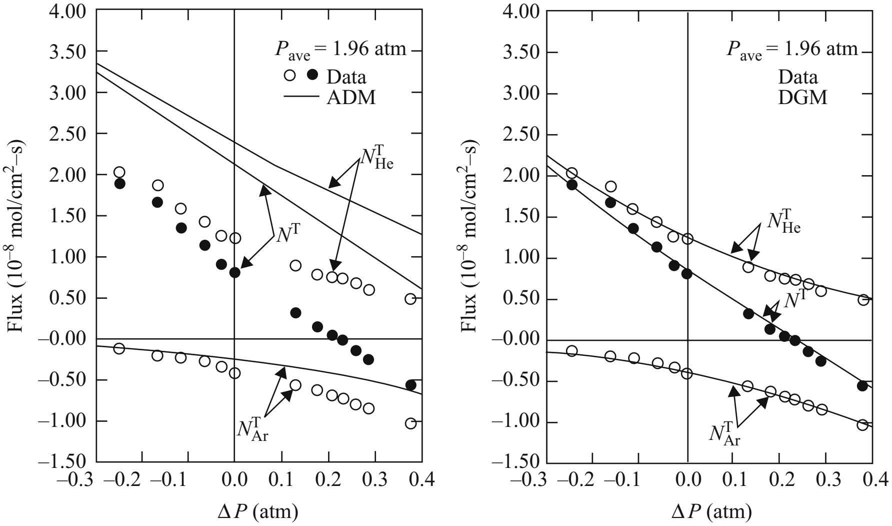
Data-model comparisons are given in Figure 2.1 as a function of the average pressure. Helium mole flux is positive, and argon mole flux is negative. The data for both gases increase with increasing pressure. The DGM data-model comparison is quite good. In addition to the individual values, the ratio of the mole fluxes is consistent with the theoretical value given above. In contrast, the model predictions of the ADM show a constant mole flux value independent of pressure for each component, which is not consistent with the data. The ADM predicts that the mass fluxes of the two components are equal. The mole flux ratio (helium/argon) is simply the inverse of the ratio of the molecular weights, or about 10, which is not consistent with the data. The ADM, which for zero pressure difference reduces to Fick's law, does not match the experimental data very well. Knudsen diffusion is not included because there isn't any advection in the ADM predictions.

2.4.2 Zero Net Mole Flux

The second case is for zero net mole flux. This case simulates what would occur in a closed volume, where the total mole fluxes of the two components are equal. The sum of diffusion and advection of each component are equal to each other resulting in a zero net mole flux. The predicted flux of each component and the pressure difference across the experiment are compared to the experimental data.

Figure 2.2a gives the data-model comparison for the mole flux as a function of the average pressure. The data-model comparison for the DGM is very good including the variation of flux with pressure. For the ADM, the predicted mole flux is constant, unlike the data.

The data-model comparison for pressure difference across the porous media is shown in Figure 2.2b. The pressure difference results in equal and opposite mole fluxes across the graphite. The data-model comparison for the DGM is very good. The ADM data-model comparison is poor, similar to the zero pressure difference case.



(a) ADM (b) DGM

Figure 2.3. Data-model comparison for combined advection and diffusion (reprinted from Webb, 1998 with permission with minor modifications)

2.4.3 Combined Advection and Diffusion

The most general situation of combined advection and diffusion is shown next. The pressure difference across the test section was varied while maintaining the same average pressure. The total individual fluxes of the two gases were measured. Figure 2.3 shows the data-model comparisons. Figure 2.3a shows the ADM comparison, which is generally poor similar to the earlier results. Figure 2.3b shows the DGM results, which show excellent agreement with the experimental data.

2.4.4 Overall Evaluation

In general, the ADM data-model comparisons are poor, while the DGM data-model comparisons are quite good. Overall, the DGM is significantly better than the ADM for the conditions of this experiment. Webb (1998) provides more details on the comparison of these two models.

Many other comparisons of the ADM, or variations of the ADM, and DGM have been performed (Abriola et al., 1992; Fen and Abriola, 2004; Oldenburg et al., 2004). All agree that for higher permeabilities, the ADM is adequate, while for lower permeabilities, the DGM is needed. Just what is "low" and "high" has not been quantified. Some guidance may be developed from the results for trace gas diffusion developed by Webb and Pruess (2003) in that the pressure and permeability were varied for different diffusing species.

2.5 TRACE GAS LIMIT

The above data-model comparison was for gas diffusion where the different gas mass fractions are significant. As shown by Webb and Pruess (2003), in the limit of trace gas diffusion in a binary mixture where one gas has a vanishingly small mass fraction, the DGM and ADM reduce to similar equations. Two “correction” factors are needed to bring the ADM in line with the DGM. The first correction factor is an additional tortuosity term on the diffusion coefficient. The second correction factor is on the Klinkenberg coefficient, *b*.

The correction factors can also be viewed as ratio of the mass flux predicted by the DGM to that predicted by the ADM. As will be seen, the tortuosity correction factor is always 1 or less, which indicates that ordinary diffusion is always overpredicted by the ADM, in some cases by orders of magnitude. The magnitude of the Klinkenberg correction factor is much smaller and may be less than or greater than 1.0 depending on the molecular weight ratio of the trace gas to the bulk species.

The standard ADM equation incorporating the Klinkenberg coefficient is as follows

$$F_g = -\frac{k_\ell}{\mu_g}\left(1+\frac{b}{\overline{P_g}}\right)\rho_g\left(\nabla P_g - \rho_g \overline{g}\right) - \rho_g D_{12}^{*}\nabla x$$

Introducing the correction factors gives

$$F_g = -\frac{k_l}{\mu_g}\left(1+\frac{b_{\mathrm{DGM}}b}{\overline{P_g}}\right)\rho_g\left(\nabla P_g - \rho_g \overline{g}\right) - \tau_{\mathrm{DGM}}\rho_g D_{12}^{*}\nabla x$$

The first term on the RHS is simply the convective flux including the Klinkenberg correction factor. The second term on the RHS is ordinary diffusion with a tortuosity correction factor. For trace gas diffusion, these factors are given by (see Webb and Pruess, 2003)

$$b_{\mathrm{DGM}} = \frac{1 + m_{\mathrm{rat}}^{1/2} D_{\mathrm{rat}}}{1 + D_{\mathrm{rat}}}$$

and

$$\tau_{\mathrm{DGM}} = \frac{1}{1 + D_{\mathrm{rat}}}$$

where D_{rat} is the ratio of the effective ordinary diffusion coefficient to the Knudsen diffusion coefficient, or

$$D_{\mathrm{rat}} = \frac{D_{12}^{*}}{D_{1K}}$$

and m_{rat} is the ratio of molecule weights

$$m_{\mathrm{rat}} = \frac{m_2}{m_1}$$

where gas 1 is the trace diffusing species and gas 2 is the bulk species.

The above expressions for b_{DGM} and τ_{DGM} have been evaluated by Webb and Pruess (2003) for a bulk species of air at 25°C and a porous media with a porosity of 0.4 and a tortuosity of 0.74. The permeability was varied over a wide range, and the trace gas species include He, water vapor, and TCE.

Figure 2.4 shows the variation in the correction factors as a function of permeability for three different trace gases (He, H_2O, and TCE) at three different gas pressures

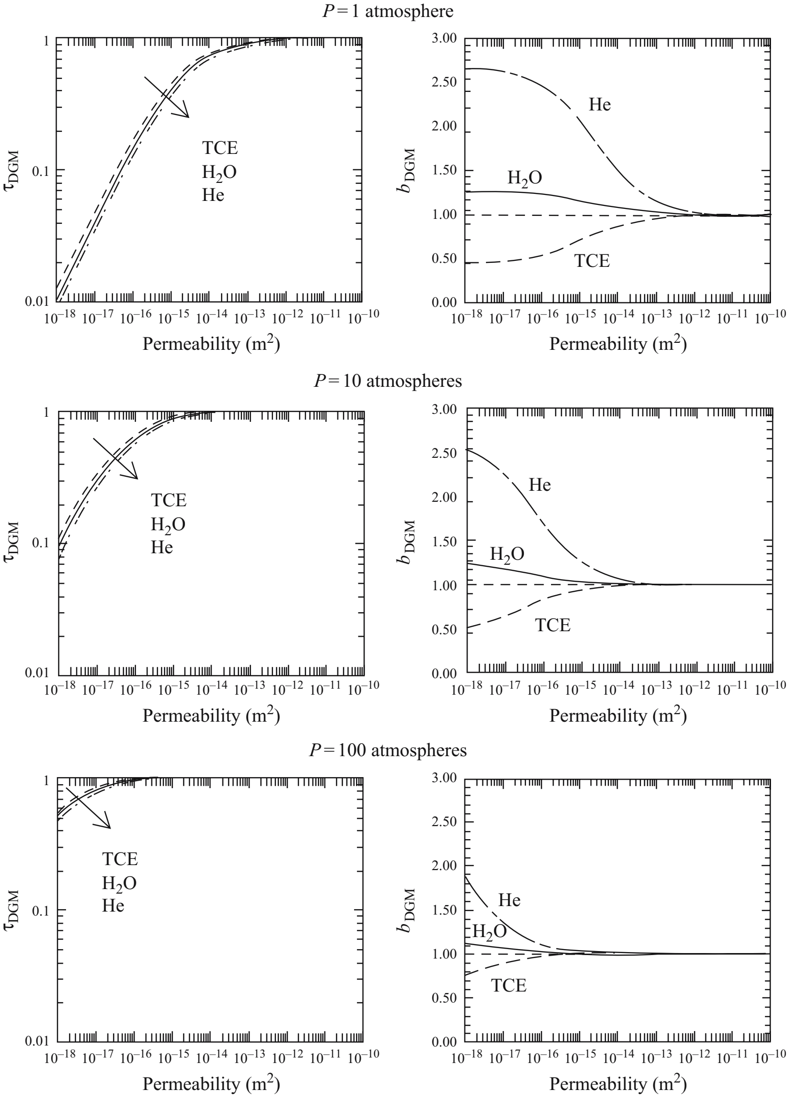


Figure 2.4. Trace gas correction factors as a function of pressure, permeability, and trace gas (reprinted from Webb and Pruess, 2003 with permission)

(1, 10, and 100 atmospheres). The b_{DGM} correction factor depends on the trace gas. If the trace gas is heavier than the bulk species (air), the correction factor is less than 1.0. Conversely, if the trace gas is lighter than the bulk gas, the b_{DGM} correction factor is greater than 1.0. The values have a generally small range, varying between about 0.5 and 2.7 for the trace gases evaluated. The τ_{DGM} correction factor can be viewed as the ratio of ordinary diffusion flux predicted by the DGM divided by the Fick's law value. For example, if the value of τ_{DGM} is 0.01, Fick's law without the correction factor would overpredict the ordinary gas diffusion flux by two orders of magnitude compared to the DGM prediction. The value of τ_{DGM} is about unity for higher permeabilities ($> 10^{-13}$ m^2) at all pressures. For lower permeabilities, Fick's law may dramatically overpredict the gas diffusion flux. The value of τ_{DGM} decreases dramatically to about 0.01 at a permeability of 10^{-18} m^2. The variation of the ratio for different trace gases is small. Therefore, the difference between the DGM and ADM becomes important for permeabilities $< 10^{-13}$ m^2, with larger differences for lower permeabilities and lower pressures.

2.6 APPLICABILITY OF DGM TO REAL POROUS MEDIA

There are questions and concerns about the applicability of the DGM to real porous media and the appropriate parameter values. While a number of authors (Abu-El-Sha'r and Abriola, 1997; Fen and Abriola, 2004; Cunningham and Williams, 1980, pg. 220; Mason and Malinauskas, 1983, pg. 50) address this point, it must be pointed out that the DGM (or the other coupled models as discussed earlier), are the best models to date and are vastly superior to the ADM, which was used for a number of years and is still used today.

While the DGM is widely used, there are modifications to improve its applicability. For example, modifications have been made to the DGM to include things such as mass transfer (e.g., Chen and Rinker, 1979) and chemical reaction (e.g., Veldsink et al., 1995). Note that these references are just representative and do not necessarily represent the latest information on these modifications.

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NOMENCLATURE

b	Klinkenberg coefficient
c	concentration
c_{F}	constant in Forchheimer equation
D	ordinary diffusion coefficient
$D_{i\mathrm{K}}$	Knudsen diffusion coefficient

F	mass flux
$\bar{g}$	gravity
J^{M}	diffusive mole flux relative to molar-average velocity value
k	permeability
m	molecular weight
N^{D}	diffusive mole flux relative to stationary coordinates
N^{T}	total mole flux relative to stationary coordinates
n	molecular density
P	pressure
$\overline{P}$	average pressure
r	radius
R	gas constant
Re_k	permeability-based Reynolds number
S	saturation
T	temperature
u	Darcy velocity
V	pore velocity
x	mole fraction

Greek

β	porous media factor
τ	tortuosity
ϕ	porosity
ρ	density
μ	viscosity
$\tilde{\mu}$	effective viscosity at wall (Brinkman equation)

Subscript

A,B	components A, B
air	value for air
CF	clear fluid
DGM	Dusty Gas Model
g	gas
K	Knudsen diffusion
ℓ	liquid phase
pore	pore
PM	porous media
rat	ratio
ref	reference
S	saturation
0	all-gas conditions
1,2	component 1, 2

Superscript

D	ordinary diffusion
K	Knudsen diffusion
T	total
$*$	effective porous media value

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