Flux Equations for Gas Diffusion in Porous Media

David B. McWhorter

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The Groundwater Project

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Dedication

This book is dedicated to the memory of Dr. Arthur T. Corey, an eminent scholar and teacher. He championed fundamentals and his emphasis on physical principles in research and teaching positively influenced countless students.

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The Groundwater Project Foreword

The United Nations Water Members and Partners establish their annual theme a few years in advance. The theme for World Water Day on March 22, 2022, is "Groundwater: making the invisible visible." This is most appropriate for the debut of the first Groundwater Project (GW-Project) books in 2020, which have the goal of making groundwater visible.

The GW-Project, a non-profit organization registered in Canada in 2019, is committed to contribute to advancement in education and brings a new approach to the creation and dissemination of knowledge for understanding and problem solving. The GW-Project operates the website https://gw-project.org/↗ as a global platform for the democratization of groundwater knowledge and is founded on the principle that:

"Knowledge should be free and the best knowledge should be free knowledge." Anonymous

The mission of the GW-Project is to provide accessible, engaging, high-quality, educational materials, free-of-charge online in many languages, to all who want to learn about groundwater and understand how groundwater relates to and sustains ecological systems and humanity. This is a new type of global educational endeavor in that it is based on volunteerism of professionals from different disciplines and includes academics, consultants and retirees. The GW-Project involves many hundreds of volunteers associated with more than 200 organizations from over 14 countries and six continents, with growing participation.

The GW-Project is an ongoing endeavor and will continue with hundreds of books being published online over the coming years, first in English and then in other languages, for downloading wherever the Internet is available. The GW-Project publications also include supporting materials such as videos, lectures, laboratory demonstrations, and learning tools in addition to providing, or linking to, public domain software for various groundwater applications supporting the educational process.

The GW-Project is a living entity, so subsequent editions of the books will be published from time to time. Users are invited to propose revisions.

We thank you for being part of the GW-Project community. We hope to hear from you about your experience with using the books and related materials. We welcome ideas and volunteers!

The GW-Project Steering Committee

May 2021

Foreword

This book: **Flux Equations for Gas Diffusion in Porous Media** concerns a topic that few groundwater scientists and engineers encounter in their education and day-to-day experience, and it fills that gap by addressing fundamental processes important to many aspects of groundwater science. Diffusion is most commonly associated with Fick's "law". Applications of Fick's law in groundwater quality are analogous to use of Darcy's "law" for groundwater flow but, in the context of subsurface processes, diffusion has more complexities than flow. Groundwater flow is founded on Darcy's equation for the relationship between flow and the hydraulic gradient and it serves us well in nearly all cases of practical relevance. However, Darcy's "law" is not universal as are the fundamental laws of physics and fluid mechanics because it is only valid for a limited range of flow conditions in porous media. Awareness of the fundamentals underlying relationships known as "laws" is essential for avoidance of confusion and errors in the solution of practical problems.

Independent of Henry Darcy's work in 1856-France, which showed that hydraulic gradient drove the flow of water in saturated porous sand, Adolf Fick's work in 1855-Germany demonstrated that concentration gradient drove the diffusive movement of chemical molecules and ions in liquids. This became known as Fick's law and is a law of fundamental importance for chemical engineering, much as Darcy's law is for groundwater science. Fick's law applies to movement of dissolved constituents in water and in water saturated porous media and serves as a building block for the development of the equations that describe diffusive movement of gaseous constituents in partially saturated porous media (i.e., the vadose zone). In groundwater geochemistry and subsurface contamination, Fick's equation is as important and, in many situations, is more important than Darcy's equation.

This book is an introduction to the fundamental processes governing the movement of gases in the vadose zone. These processes are key to understanding important topics such as the fate of petroleum products that leak into the subsurface and how harmful vapors from toxic chemicals move through the vadose zone to cause deterioration of indoor air. Moreover, this book examines how the movement of gases in the vadose zone came to be correctly understood in the context of both Fick's law of diffusion and Graham's law of gas diffusion. Although the behavior of gases in porous media has been the subject of scientific scrutiny and engineering applications for more than a century, it was not until the middle part of the twentieth century that clarity of understanding emerged in the fields of physical chemistry and chemical engineering, yet confusion persists about how the fundamental processes apply to problems concerning subsurface contamination. This book is an examination of the intellectual journey from confusion to clarity, which began nearly two centuries ago with the work of Thomas Graham in 1833. This journey is akin to a scientific detective story.

David McWhorter is an emeritus professor of Colorado State University who, early in his career, authored a textbook on groundwater hydraulics. His career then focused on research into the fundamental processes of movement and fate of oily liquids and solutes in the subsurface and the application of his finding to groundwater contamination problems.

John Cherry, Groundwater Project Leader

Guelph, Ontario, Canada, May 2021

Preface

The author's interest in gas diffusion in porous media was triggered by Dr. John Farr when, as an advisee, he questioned how Fick's first law of diffusion and Graham's law of diffusion could be reconciled. A significant relevant literature was found to exist in physics, chemical physics and chemical engineering, but few of the findings in these fields have so far widely penetrated the earth sciences. A goal of this book is to improve the awareness on the part of earth scientists and engineers of the depth of knowledge that exists on this subject and to foster a better understanding of one of the fundamental transport processes that operates beneath the Earth's surface.

Acknowledgements

David B. McWhorter

1   Introduction

Subsurface fluids are a mixture of multiple constituents. Vadose zone gas often contains nitrogen, oxygen, carbon dioxide, argon, water vapor, and, perhaps, vapors from volatile liquids (e.g., gasoline, solvents). Other GW-Project books are concerned with fluid motion as described by Darcy's law, which calculates the motion of a mixture without regard to composition. But individual species in fluids of non-uniform composition experience motion that is in addition to that imparted by viscous flow and is subject to different driving and resisting forces. This additional increment of motion is called diffusion and is the subject of this book.

Diffusion in the gas phase is an important phenomenon in a variety of problems important to earth scientists and engineers. For example, the supply and elimination of gases to and from the root zones of plants is affected by diffusion in soil gas and is studied by soil and plant scientists. Hydrogeologists, engineers, and environmental scientists are interested in the migration of vapors from volatile sources of contamination lodged in the vadose zone. Among the concerns is the creation of a migrating vapor plume in the vadose zone that might act as a source of groundwater contamination via partitioning of chemicals from the gas phase to contiguous groundwater. Diffusion in the gas phase is partially responsible for the so-called vapor intrusion problem, where contaminated air in basements and crawl spaces of buildings can be linked to subsurface sources as indicated in the cover figure of this book. Diffusion of contaminants from low permeability strata may influence the performance and efficacy of soil-vapor extraction systems. Natural degradation of liquid petroleum present in the vadose zone often generates diffusive fluxes of gases such as oxygen, carbon dioxide, and methane. Analysis and measurement of such diffusive fluxes sometimes assists in the estimation of the rates of natural degradation and the projection of source longevity. Emanation of gases from landfills is yet another circumstance in which diffusion in the gas phase plays an important role.

1.1   What is Diffusion?

The molecules in a gas are in constant, chaotic thermal motion. Because the molecules are free to move about, they continually intermingle and collide with one another. While the kinetic energy of individual molecules is variable, the average kinetic energy of molecules in a gas at uniform temperature is constant, even if the gas is made up of multiple species with different molecular masses. Massive molecules move more slowly than do lighter molecules by just the amount necessary to make the kinetic energies equal on average.

Because the average kinetic energies of all constituent species are the same in a gas at constant temperature, a non-uniform distribution of constituent species as indicated by variable concentration does not result in a variable distribution of kinetic energies for the

gas as a whole. On the other hand, variable constituent concentration (i.e., variable number of molecules per unit volume) means that the average kinetic energy of individual components is correspondingly non-uniform. Molecules of individual constituents migrate from positions where the local average constituent kinetic energy is high to positions where it is low. This migration is diffusion.

The intermingling of two gases in a diffusion chamber located between supply headers at the same pressure is depicted in Figure 1a. Because there is no pressure difference across the chamber between headers *A* and *B*, only diffusion is responsible for any transport that occurs. As gases *A* and *B* intermingle (diffuse into one another) they form a single gas with two components. The mixture is referred to as a binary gas. The constituents of the binary gas diffuse from their respective sources in the direction of decreasing concentration. The diffusive motion is the translation of an aggregate of molecules and may be expressed as a rate of flow measured in moles, volume, or mass per unit time.

Suppose we were to conduct an experiment in which steady diffusion of a binary gas at uniform temperature and pressure occurs in this chamber that connects headers at identical pressures (Figure 1a). First, consider the case in which the diffusion chamber is devoid of solid particles. In this case, the only impediment to diffusion of each constituent is that which arises from the collision with molecules of the other constituent (collisions with the walls of the large diameter chamber are neglected). It is diffusion of this kind that is most commonly treated in text books (e.g., Bird et al., 2002; Cussler, 1997) and for which Fick's law (Fick, 1855) applies (see Section 2.4 for a presentation of Fick's law). Both experimental observation and Fick's law show that the two components of the binary gas diffuse into one another at equal rates and in opposite directions, even though the molecular weights may be different. Thus, the diffusive fluxes of the constituents mutually cancel and the binary gas, as a whole, experiences no net motion. This kind of diffusion is often referred to as ordinary diffusion.
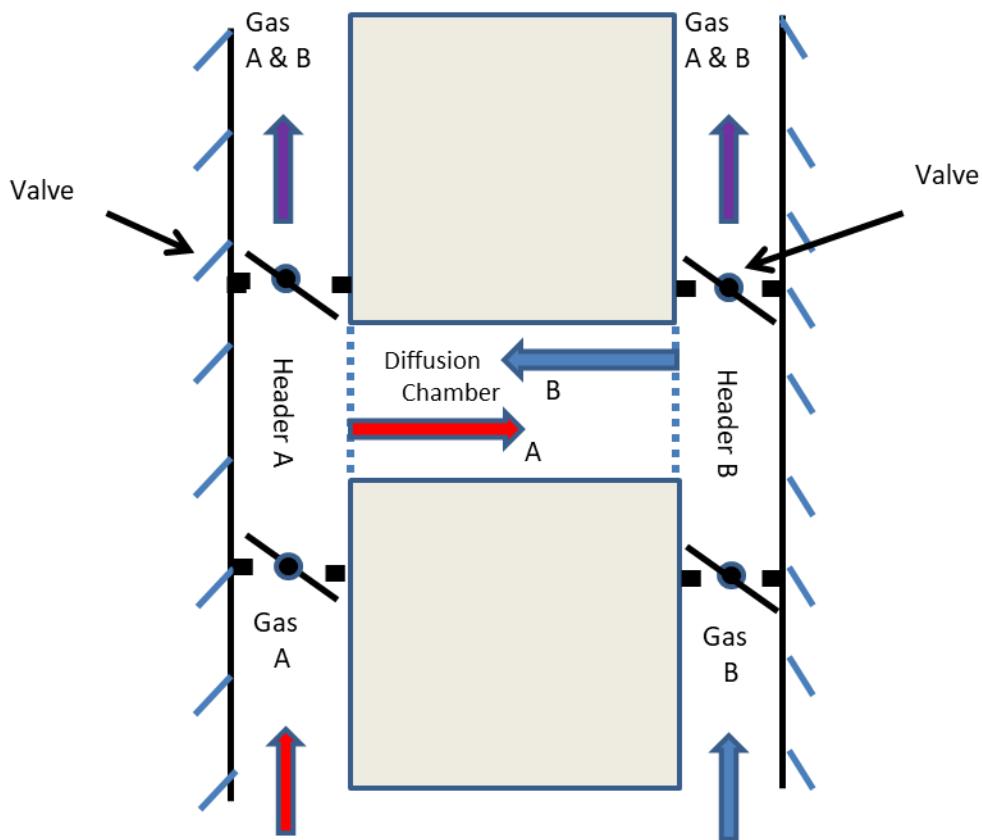
Figure 1a - A thought experiment for steady binary diffusion between headers at identical pressures. Gas A is introduced in the left-hand header, diffuses through the chamber toward the right, and is exhausted in the mixture at the top of the right-hand header. Gas B, introduced in the right-hand header, diffuses toward the left, and is exhausted as part of the mixture at the top of the left-hand header. The concentrations of gas A in the exhaust from the right header and of gas B from the left header are minimized by large flow rates in the headers. Gases A and B diffuse at the same rates and in opposite directions.

Now consider a second experiment in which diffusion occurs in the chamber after it was filled with sand (Figure 1b). An obvious effect of filling the diffusion chamber with sand is that the cross-sectional area available for gas-phase diffusion is reduced. Also, the sand causes the diffusion path to be tortuous and, therefore, longer than in the first experiment. These obstructions equally effect diffusion of both components and do not account for the surprising fact that the diffusion rates of the two constituents are generally observed to be of unequal magnitude and no longer mutually cancel. One manifestation of the unequal diffusion rates is a bulk flow of the binary gas in the direction of diffusion of the component with the lower molecular weight. This diffusion-generated bulk flow occurs even though there is no pressure gradient. The commonly held notion that viscous flow and flow of the fluid as a whole are synonymous is not true for binary gases in a porous medium.
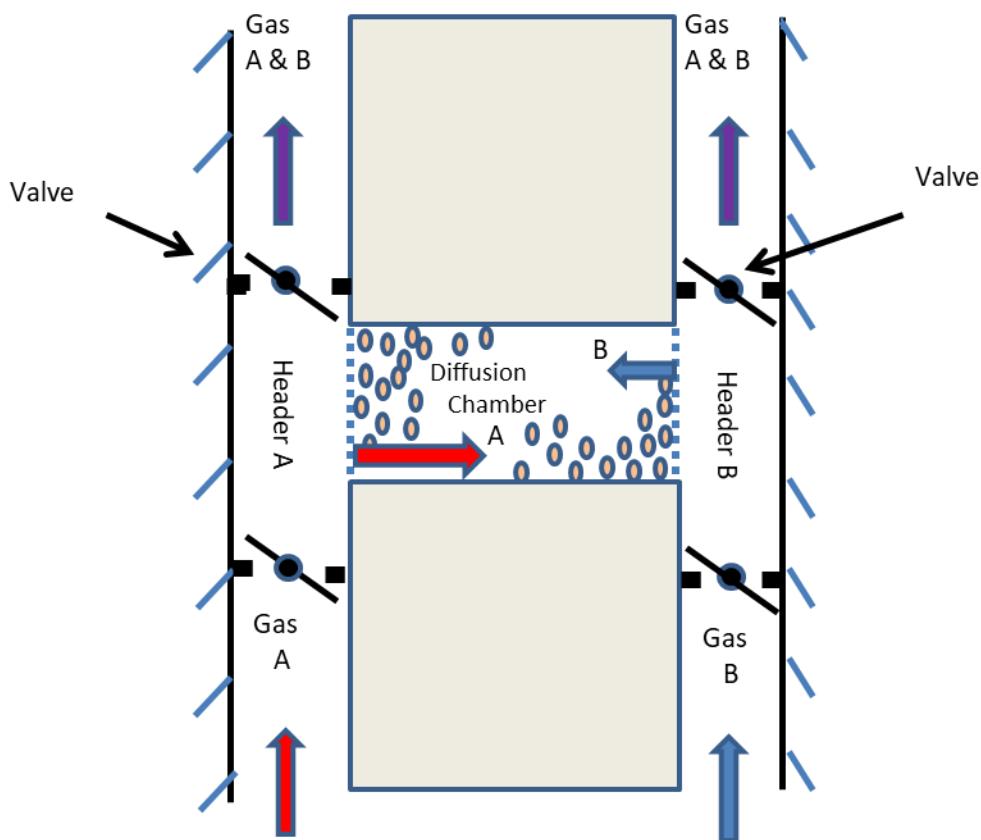
Figure 1b - Steady binary diffusion in a particle-filled chamber. Gas A has a lower molecular weight and diffuses more rapidly to the right than does gas B to the left, as indicated by the arrows.

Yet another unexpected feature of gas diffusion in porous media is the coupling that exists between diffusion and viscous flow. Should all the valves in the apparatus shown in Figure 1b be simultaneously closed at some point during the second experiment, a pressure gradient develops that drives bulk gas flow in the direction opposing the diffusion-generated bulk flow. This feature of diffusion does not occur if the diffusion chamber is free of solid particles and wall effects are negligible. This is another manifestation of how the presence of solid particles affects diffusion in profound and fundamental ways.

1.2   A Brief History of Diffusion Science

The tortuous history of the development of today's understanding of the above phenomena and other aspects of the theory of diffusion of gases in porous solids is described in detail by Cunningham and Williams (1980). It is a fascinating story that chronicles the major developments in the science of diffusion and analyzes in some depth the many mistakes and misconceptions that occurred along the way. The story begins with Thomas Graham (1833), who observed and reported with little explanation all of the phenomena described in the above discussion. Graham also conducted experiments on diffusion in liquids, the results of which were an important contribution to the

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development of the first constitutive equation for diffusion, now known as Fick's law (Fick, 1855).

For the next 100 years, Fick's law was commonly thought to be the only constitutive equation necessary to codify the results of diffusion experiments. Fick's law, developed for diffusion in liquids but often assumed to apply to gases as well, predicts that the components of an isobaric binary gas diffuse at equal rates in opposite directions and that no diffusion-engendered bulk flow occurs. While this prediction was inconsistent with Graham's results, it was apparently correct in other experiments performed under different working conditions. Consequently, Graham's results came to be discredited and were generally ignored or forgotten until the middle of the twentieth century when they were resurrected by Hoogschagen (1955). The simple empirical equation that conveniently expresses the salient result of Graham's experiments was eventually elevated to the status of a law on par with Fick's law and is now known as Graham's law of diffusion.

An important advance in the theoretical study of diffusion in gases occurred during the second half of the nineteenth century. According to Cussler (1997), Clerk Maxwell recognized as early as 1860 that diffusion generates bulk flow. He modified Fick's law to include advection by diffusion-engendered bulk flow and interpreted the equation in terms of the rate of momentum loss of a component due to molecular collisions of that component with molecules of the second species (Cunningham and Williams, 1980). Hoogschagen (1955), who was evidently unaware of Graham's work, conducted independent experiments that showed the mole fluxes of the individual components were related to each other in the manner discovered by Graham. He combined what is now known as Graham's law with Maxwell's constitutive equation to derive the first correct expression for steady diffusion in an isobaric, binary gas occupying the voids of a porous medium.

Hoogschagen's expression for isobaric diffusion applies when the resistance to diffusion is dominated by the collisions between the molecules of one component with those of the other. This is the situation that prevails in the so-called molecular regime. It was yet another several years before the theory of diffusion in gases in porous media was extended by E. A. Mason and coworkers (Evans III et al., 1961, 1962; Mason et al., 1967; Mason and Malinauskas, 1983) to include the resistance to diffusion that results from collisions of component molecules with solid particles embedded in the diffusion path. This prodigious work culminated in what is now known as the Dusty Gas Model, in which solid particles embedded in the system are regarded as giant immobile molecules. The Dusty Gas Model includes rigorously derived constitutive equations for multi-component transport in porous solids, together with physical interpretations and predictive expressions for the transport coefficients that emerge. The Dusty Gas Model constitutive equation for diffusion reduces to the familiar Fick's law only under very restrictive conditions.

1.3   Scope

Detailed presentations of the development of the Dusty Gas Model are provided in Cunningham and Williams (1980) and Mason and Malinauskas (1983). Key ideas of the Dusty Gas Model can be incorporated in a simpler "phenomenological" approach to diffusion that fosters physical insight and understanding at a level between a simple recitation of the equations and the in-depth physics and mathematics in the original scientific papers (Cunningham and Williams (1980). Most of the developments in the present book are drawn from Cunningham and Williams. However, the considerations in this book are limited to one-dimensional transport of ideal, binary gases at constant temperature. This is a special case that enables by relatively simple calculation the exploration of gaseous diffusion in porous solids, a fascinating but often confusing subject. First courses in calculus, physics, and physical chemistry provide an adequate foundation for understanding the developments in this book.

2   Definition of Fluxes

Key to the understanding and analysis of diffusion is the careful consideration of the various fluxes involved in the transport processes. In general, the flux of some entity is the quantity of that entity that passes through a unit area per unit time, the unit area being oriented normal to the direction of the flux. Because we are working with porous media, the area referred to here is the bulk or total area. The bulk area is generally comprised of portions occupied by solids, liquids, and gas. Flux defined in this way is a macroscopic quantity in the same sense that specific discharge of groundwater is a macroscopic quantity.

Flux can be in reference to many different entities (e.g., electrical current, energy, heat, water, and other entities that are commonly transported). We will have occasion to use fluxes that reference volume, mass, moles and momentum, but we have selected moles of gas as our reference quantity for calculating flux and concentration in the central developments of this book. Developments entirely parallel to those in this book can be made using mass flux and mass concentration. Flux is, in general, a multi-component vector. In the interest of simplicity, we limit our treatment to transport along one coordinate, so the flux can be considered a scalar that may be positive or negative, depending upon direction.

The mole flux (moles per unit bulk area per unit time) of an individual component, say species i, of a mixture is given the symbol N_i. The mole flux of the mixture as a whole is denoted by N and is the sum of the component mole fluxes $N = \Sigma_i N_i$, $i = A, B$. Therefore, N is the flux of gas as a whole (i.e., the phase motion). Recall the discussion of the second experiment relating to Figure 1b in which we observed that diffusion engenders bulk gas flow that is not driven by a pressure gradient. For this reason, we purposely do not equate phase motion with the viscous flow calculated by Darcy's law.

Gas flow calculated by Darcy's law is only one contributor to flow of the phase, a concept that will likely be foreign and seem incredible to those encountering it for the first time.

2.1   Viscous Flux

The viscous flux appearing throughout this book is the volume flux calculated by Darcy's law. This calculation is most familiar in the context of water flow and appears in various forms throughout the GW-Project books. Here, we express Darcy's law in a form suitable for the calculation of the viscous contribution to the flow of the gas phase. As is the case for water and other fluids, the driving forces are the pressure gradient and the body force due to gravity. The latter may be important when the gas column of interest is very thick (Thorstenson and Pollock, 1989), but we include only the pressure gradient in the following developments and write Darcy's law as Equation 1.

$$v = - \frac{k_g}{\mu} dp/dl \qquad (1)$$

where:

v = macroscopic volume flux (specific discharge, $L^3/L^2 T = L/T$)

p = pressure of the gas (F/L^2)

l = coordinate along which the motion occurs (L)

μ = dynamic viscosity (FT/L^2) (which we treat as a constant in all subsequent developments)

k_g = permeability to gas $\left(L^2\right)$ (associated with the resistance to gas motion that arises solely from viscous shear at the pore scale)

The subscript, g, distinguishes the gas permeability (k_g, also known as effective permeability) from the intrinsic permeability, k, of the porous medium. This distinction is required because the co-existence of liquids in the pore space causes the gas permeability to be smaller than the intrinsic permeability, sometimes dramatically so (e.g., Brooks and Corey, 1966). The gas permeability k_g is equal to the intrinsic permeability when the porous medium is dry. The reduction in gas permeability due to the presence of liquid in the pore space is related to the concepts of effective and relative permeability as described by Corey (1994).

Multiplication of v by the total molar concentration of the gas C (total moles of all components per unit volume), followed by use of the ideal gas law, $p = RTC$, wherein R is the gas constant (FL/moles T) and T is absolute temperature, gives Equation 2 for the viscous mole flux of the gas phase.

$$N^v = - \frac{k_g p}{\mu RT} \frac{dp}{dl} = - \frac{k_g p}{\mu} \frac{dC}{dl} \qquad (2)$$

The flux calculated by Equation 2 is a contributor to the motion of the mixture as a whole. Being a component of the mixture, an individual species is carried along (advected) by the

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viscous contribution to the phase motion. The advection mole flux of an individual species due to the viscous flux is calculated according to $N_i^v = x_i N^v$, $i = A, B$ where x_i is the mole fraction of component i in the mixture. The mole fraction is defined by $x_i = C_i/C$, where C_i is the molar concentration of constituent i. The sum of mole fractions over all constituents is always unity.

2.2   Total Diffusion Flux

The flux calculated by Equation 2 is referred to as a viscous flux because the resistance to the fluid motion results from viscous shear. Diffusive motion is not resisted by viscous shear. Diffusion of a component in a gas mixture is defined as the increment of motion that is in addition to that imparted by the viscous motion. Thus, the overall or total flux of an individual constituent is given by Equation 3.

$$N_i = N_i^D + N_i^v \quad i = A, B \tag{3}$$

Equation 3 defines diffusion as the increment of motion of constituents that is in addition to the motion imparted by advection in viscous flow. The first term on the right of Equation 3 is referred to as the total diffusion flux of component i and the second is the contribution to the flux of component i that results from advection via the viscous contribution to the motion of the phase. We will learn in later developments that the total diffusion term includes advection of species i by the diffusion-generated contribution to bulk flow.

The sum of N_i for $i = A, B$ gives the flux of the gas as a whole as expressed in Equation 4.

$$N = N^D + N^v \tag{4}$$

The flux of the gas phase as a whole is due to both diffusion and viscous flow. Again, those who are used to thinking of binary diffusion as a process in which the diffusion fluxes of the constituents are of equal magnitude and opposite in sign will find Equation 4 unfamiliar.

Readers familiar with the traditional treatment of transport of dissolved constituents in groundwater may wonder why Equation 3 doesn't contain a term representing mechanical dispersion. Non-uniform advection at the pore scale creates pore-scale concentration gradients that are manifest at the macroscopic scale by spreading or dispersal of species that is in addition to that attributable to diffusion alone. This extra increment of spreading is known as mechanical dispersion and is readily observable in solute transport in groundwater. However, multi-dimensional diffusion at the pore scale acts to smooth the variable concentration created by non-uniform advection and, thus, reduces mechanical dispersion. In the case of gases, where diffusion coefficients are typically 1000 times greater than for solutes in liquids, mechanical dispersion is not likely

to be an important spreading mechanism relative to macroscopic diffusion. For this reason, a term representing mechanical dispersive flux is not included in Equation 3.

2.3   Fluxes That Comprise Total Diffusion Flux

Graham's (1833) experiments clearly demonstrate that the components of a binary gas at uniform pressure in a porous medium diffuse at different rates in general. Consequently, the sum of the total diffusive fluxes of the individual components, $N_A^D + N_B^D$, is not zero. Rather, this sum contributes to the motion of the fluid as a whole—a feature of diffusion in porous solids that is not observable in systems free of solid obstructions. We refer to this net diffusive flux as the non-equimolar flux (Cunningham and Williams, 1980) and write Equation 5.

$$N^D = N_A^D + N_B^D \tag{5}$$

Similar to the viscous flux, the non-equimolar flux imparts motion to the individual species in the mixture by advection (i.e., $x_i N^D$, $i = A, B$), but is distinguished from advection via a viscous flux by the fact it arises solely as a result of diffusion. The sum of advection by the non-equimolar flux and by the viscous flux is the total advection by the phase motion.

The increment of motion for component i that is in addition to advection via the phase motion is the equimolar diffusion flux J_i defined by Equation 6.

$$J_i = N_i - x_i N \quad i = A, B \tag{6}$$

Because equimolar diffusion makes no net contribution to motion of the phase, we have Equation 7.

$$J_A + J_B = 0 \tag{7}$$

Equation 7 expresses a condition that holds under all circumstances treated in this book.

It is common to rearrange Equation 6 so that the mole flux is expressed as the sum of the equimolar and advection fluxes as in Equation 8a for constituent A. We may then express the flux of component A by any one of Equations 8a through 8d. The subscripts can be interchanged to obtain the equivalent expressions for component B.

$$N_A = J_A + x_A N \tag{8a}$$

$$N_A = J_A + x_A(N_A + N_B) \tag{8b}$$

$$N_A = J_A + x_A(N^D + N^v) \tag{8c}$$

$$N_A = J_A + x_A(N_A^D + N_B^D + N^v) \tag{8d}$$

The reader is encouraged to become thoroughly familiar with these definitional equations and the various forms they may take. For example, if there is no viscous flux then $N^v = 0$, $N_A = N_A^D$ and Equation 8d becomes Equation 9.

$$N_A^D = J_A + x_A(N_A^D + N_B^D) \tag{9}$$

Rearranging and solving for J_A gives Equation 10.

$$J_A = N_A^D x_B - x_A N_B^D \tag{10}$$

This is in the form of a Stefan-Maxwell equation for a binary gas that we soon will have occasion to use in our calculations.

2.4   Fick's Law

Fick's first law of diffusion (Fick, 1855) is a central feature of practically all discussions of diffusion. A variety of mathematical expressions for Fick's law that calculate different fluxes using different forms of concentration gradient are present in the literature. Not all of these expressions are equivalent to one another. We have elected in this book to carry out all of our developments in terms of molar fluxes and concentrations. In that notation, only Equation 11 is referred to as Fick's law from this point forward.

$$J_i = -D\,C\,dx_i/dl \quad i = A, B \tag{11}$$

The flux calculated by Equation 11 is the equimolar flux defined by Equation 10. The parameter D is the effective diffusion coefficient (L^2/T), a modification of the molecular diffusion coefficient, D_m (L^2/T), to account for the reduction of cross-sectional area available for gas diffusion and the increase in diffusion path length caused by the presence of solids and liquids (see Section 6). If there are no obstructions then the effective diffusion coefficient is equal to the molecular diffusion coefficient available in handbooks. We set aside for the time being any further discussion of the physical ingredients of D and D_m except to note that the coefficient pertaining to diffusion of A into B is the same as for B into A. Further, kinetic theory predicts that this binary molecular diffusion coefficient is inversely proportional to the gas pressure. It is clear from Equation 33 in Section 6 that these characteristics of the molecular diffusion coefficient are true of the effective diffusion coefficient as well.

Importantly, Equation 11 satisfies Equation 7, a condition that is not restricted to isobaric diffusion. That is, Fick's law in this book calculates the equimolar fluxes in either an isobaric or non-isobaric binary system. Many authors assume $J_i = -D\,dC_i/dl$ as the form for Fick's law (or the equivalent form on a mass basis). However, this form is not consistent with the flux definitions presented herein; in particular Equation 10 is not satisfied by this alternate form when the diffusion is influenced by a pressure gradient. We regard Equation 11 as the more general form, applicable for both liquids and gases under either isobaric or non-isobaric conditions.

3   Driving Forces for Diffusion

Consider a container (Figure 2a) of an ideal binary gas at uniform temperature, pressure and composition. On average, all of the molecules in the binary gas have the same kinetic energy because the temperature is uniform. Let us imagine a plane across the container so that it is divided into two sections as shown. Molecules of both components continuously pass back and forth across the plane due to their random thermally induced motion. We may also think of the dividing plane as a wall against which the molecules on either side collide. These collisions are responsible for exerting pressure on the wall. If the number of molecules per unit volume on both sides of the surface is the same, there is no pressure difference across the surface. The pressure created by molecules on one side is opposed by an equal pressure in the gas on the other. The contribution to total pressure made by an individual component is known as the partial pressure, p_i, of that component. The partial pressure of each component is related to the component molar concentration by $p_i = C_iRT$.
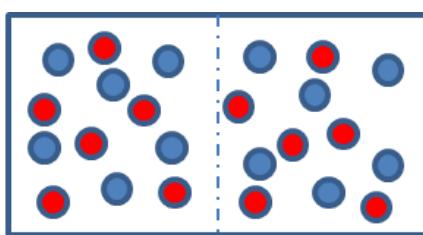
Figure 2a - Binary   gas   at   uniform composition, pressure and temperature.

Now suppose the composition of the binary gas is changed by removing from the left side some molecules of species *A* and replacing them with the same number of species-*B* molecules. The concentration of species-*A* molecules is now less on the left than on the right and the opposite is true for species *B* (Figure 2b). The total pressure on either side of our imaginary surface is unchanged because the total number of molecules is still the same on both sides of the surface. However, the number of *A* molecules impinging on the imaginary surface from the left is less than from the right and the opposite is true for *B* molecules. Thus, there is a net diffusion of species *A* from right to left and species *B* experiences a net diffusion from left to right. In both cases, diffusion occurs from high to low concentration or, equivalently, from high partial pressure to low partial pressure. Some authors employ differences in the thermodynamic quantity known as chemical potential (energy per mole) as the indicator of the direction of diffusion. However, concentration, partial pressure, and chemical potential are closely related quantities in isothermal ideal gases and each can be used to indicate the direction of component diffusion when the composition is not uniform.
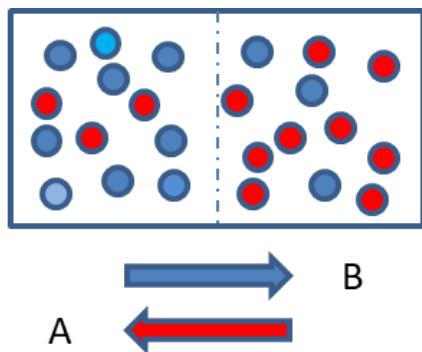
Figure 2b - Binary gas with non-uniform composition. Molecules A diffuse to the left and molecules B diffuse to the right.

The gradient of concentration, partial pressure, or chemical potential may be used to express the driving force for the diffusion described in the previous paragraph. We choose to use the gradient of partial pressure for the moment because it has dimensions of force per unit volume and makes the discussion of momentum balances in the following section more intuitive and easier to grasp. It is important to note that the gradient of partial pressure is not an external force that acts on the fluid as a whole; rather, the gradient of partial pressure of a component is an internal force that drives diffusion of that component. The partial pressure of component i is related to the total gas pressure and the component mole fraction by $p_i = px_i$. The gradient of partial pressure is expressed below in Equation 12.

$$\frac{dp_i}{dl} = p\frac{dx_i}{dl} + x_i\frac{dp}{dl} \tag{12}$$

It follows that the driving force for diffusion of an individual component is affected by both a gradient of mole fraction and a pressure gradient in the gas as a whole. Of course, a pressure gradient also induces bulk gas flow, but the second term on the right side of Equation 12 derives from the gradient of partial pressure in the present context and is a force driving diffusion. Diffusion in response to the gradient of total gas pressure is often referred to as pressure diffusion.

4   Resistance to Diffusion

It is well known that the resistance to viscous flow in porous media primarily arises from viscous shear as the fluid makes its way through small, tortuous channels left open among the collection of solid particles. In contrast, diffusion occurs without loss of momentum by viscous shear. Nevertheless, diffusing species undergo a momentum change through collisions with other species and with solid particles. Resistance to diffusion arises from these collisions and the consequent change in momentum.

4.1   Momentum Balance in a Particle-Free System

Newton's law of motion relevant to the present discussion can be simply stated: the sum of the forces acting to drive motion is equal in magnitude and opposite in direction to the sum of the forces acting to resist the motion. It is helpful to examine the familiar Darcy's law in the context of this principle before undertaking the application to diffusion. Equation 1 can be rearranged to *-dp/dl = vμ/k$_g$*. In this form the left side is the driving force per unit volume and the right side is the force per unit volume that resists the motion. The quantity on the right is a macroscopic manifestation of the pore-scale rate of momentum loss per unit volume due to viscous shear within the complex and unknowable geometry of the pore space (Hubbert, 1956; Corey, 1994).

In a similar way, Fick's law represents a macroscopic momentum balance for diffusion in systems free of any solid particles or other obstructions. The interpretation of Fick's law as a momentum balance (i.e., force balance) is easier to grasp if Equation 11 is written in terms of the gradient of partial pressure. For species *A*, we obtain Equation 13.

$$-\frac{dP_A}{dl} = \frac{RTJ_A}{D_m} \tag{13}$$

The molecular diffusion coefficient is used here because there are no obstructions in the case under discussion. The left side of Equation 13 is the driving force per unit volume and the right side is the resisting force per unit volume or, equivalently, the rate of change of momentum per unit volume for species *A* due intermolecular collisions with species *B* within a local volume element. The molecular diffusion coefficient, D_m, is the phenomenological parameter that accounts for the complicated, unresolved molecular-scale process of intermolecular collisions within the volume element, just as the permeability appearing in Darcy's law is the macroscopic manifestation of the process of viscous shear that occurs in the complex geometry of internal pore space.

In this case of binary diffusion in space free of solid particles, the only mechanism by which the momentum of component *A* can be lost is through momentum exchange with component *B*. In the absence of solid particles, there can be no momentum loss by molecule-particle collisions or by viscous shear. Thus, *P$_A$ + P$_B$ = P = constant* and the only driving force for the flux, *J$_i$, i = A, B* is proportional to the gradient of the mole fraction as given in Equation 11. As mentioned previously, *J$_A$ + J$_B$ = 0*, as required by Equation 7. We now see that this means that intermolecular collisions do not contribute to a change in the momentum of the gas as a whole.

4.2   Effect of Solid Particles Embedded in the Gas

Diffusing species in a gas-particle mixture experience resistance that is the sum of that due to molecule-molecule collisions and molecule-solid collisions. Equation 14 adds the rate of momentum loss due to molecule-particle collisions (second term on the right) to the rate of momentum loss due to molecule-molecule collisions (first term on the right).

$$-\frac{dP_A}{dl} = \frac{RTJ_A}{D} + \frac{RTN_A^D}{D_A^K} \qquad (14)$$

where:

N_A^D =   total diffusive mole flux of component *A* (mol / L^2)

D_A^K =   effective Knudsen diffusion coefficient for component *A* (L^2/T)

Equation 14 is of central importance to the developments in this book and warrants further discussion.

Note from Equation 10 that the flux, J_A, appearing on the right side of Equation 14, is a function of the mole fluxes of both constituents *A* and *B*; hence, it can be concluded that the rate of momentum change for species *A* due to intermolecular collisions depends upon the flux of both constituents. Now suppose that we regard the solid particles to be giant, stationary molecules, as did the authors of the Dusty Gas Model. Then the second term on the right is conceptually the same as the first term, but with the flux of one constituent, the giant molecules (solid particles), equal to zero (Cunningham and Williams, 1980).

We use the effective diffusion coefficient, *D*, in the first term on the right of Equation 14 because particles are obstructing the diffusion space in this case. The parameter D_A^K appearing in the second term is known as the effective Knudsen diffusion coefficient in honor of Martin Knudsen, a pioneer in the study of molecule-solid collisions. As is the case for the effective molecular diffusion coefficient, the effective Knudsen diffusion coefficient is the macroscopic manifestation of molecular-scale momentum exchange, but in this case due to molecule-solid collisions instead of intermolecular collisions. Note that the Knudsen coefficient is species specific, i.e., the effective Knudsen diffusion coefficient for species *A* is different than for species *B*. This is because the molecule-particle collisions of a particular species are independent of the presence of other diffusing species. The determination of effective molecular and Knudsen diffusion coefficients is discussed in the section on parameter estimation.

It might seem that conservation of momentum should dictate zero loss of momentum when the molecules elastically collide with massive immobile particles. Indeed, such would be the case for smooth particles on which the angle of reflection is equal to the angle of incidence for all collisions (specular reflection). On the other hand, Cunningham and Williams (1980) argue that reflection of molecules impinging on a macroscopic element of rough surface (rough at the molecular scale) are chaotically reflected (diffuse reflection) when viewed at the scale of the surface element as a whole. According to these authors "… in contrast to the situation with smooth walls, the gas will lose momentum as it flows along a rough wall".

4.3   Momentum Balance for the Gas as a Whole

The momentum balance for component B is obtained from Equation 14 by replacing the subscript A with B to obtain Equation 15.

$$\frac{dP_B}{dl} = \frac{RTJ_B}{D} + \frac{RTN_B^D}{D_B^K} \tag{15}$$

The sum of Equations 14 and 15 for the individual components is the momentum balance for the gas as a whole, and is given by Equation 16.

$$-\frac{dp}{dl} = RT\left\{\frac{N_A^D}{D_A^K} + \frac{N_B^D}{D_B^K}\right\} \tag{16}$$

The first term on the right side of Equation 14 and Equation 15 sum to zero as required by Equation 7, and is an expression of conservation of momentum for intermolecular collisions within the gas, as a whole as noted previously. Thus, Equation 16 expresses the momentum balance for diffusion-initiated, molecule-particle collisions for the gas as a whole. No momentum loss due to viscous shear is accounted for in Equation 16. Under isobaric conditions Equation 16 becomes Equation 17.

$$\frac{N_B^D}{N_A^D} = -\frac{D_B^K}{D_A^K} \tag{17}$$

4.4   Graham's Law

Conservation of momentum for collisions between gas molecules and solid particles for an isobaric gas as a whole means that, on average, momentum transferred to particles by species A must be equal in magnitude and opposite in direction to that transferred by species B. The rate of momentum exchanged with the solids for each species is proportional to $N_i^D m_i \bar{v}_i$ $i = A, B$, wherein m_i is the molecular mass and $\bar{v}_i$ is the mean molecular speed. Therefore, the momentum balance is expressed by Equation 18.

$$N_A^D m_A \bar{v}_A + N_B^D m_B \bar{v}_B = 0 \tag{18}$$

From kinetic theory, the average values of molecular speed are inversely proportional to the square root of their respective molecular masses. Hence, Equations 17 and 18, together, provide the important result given by Equation 19.

$$\frac{D_B^K}{D_A^K} = \left(\frac{M_A}{M_B}\right)^{0.5} = (M_{AB})^{0.5} \tag{19}$$

where:

      M_A = molecular weight of A (mass / mol)

      M_B = molecular weight of B (mass / mol)

      M_{AB} = ratio of molecular weights of A to B, M_A/M_B, (dimensionless)

In Equation 19, molecular weights M_i, $i = A, B$, are used in place of molecular masses and M_{AB} denotes the ratio M_A/M_B. Prescription of the isobaric condition in our development is a

sufficient condition for Equation 19, but not a necessary one. The more rigorous Dusty Gas Model development shows the Knudsen diffusion coefficients are inversely proportional to the square root of the respective molecular masses and that Equation 19 holds for both constant and variable pressure (Cunningham and Williams, 1980).

A rearrangement of Equation 16, together with the use of Equation 19 and the ideal gas law, results in Equation 20.

$$N_B^D = -D_B^K \, dC/dl - (M_{AB})^{0.5} N_A^D \tag{20}$$

This shows in compact form the coupling that exists between the total diffusive fluxes when the pressure is not uniform. Even under isobaric conditions (i.e., constant C), these fluxes remain coupled, but by the simpler expression of Equation 21.

$$N_B^D = -(M_{AB})^{0.5} N_A^D \tag{21}$$

Equation 21 is known as Graham's law of diffusion. In what could be the earliest scientific investigation of diffusion, Thomas Graham (1833) studied steady counter-current diffusion of the components of binary gases through a porous plug under uniform temperature and pressure. Uniform pressure was achieved by frequent adjustment of the pressure on the face of the porous plug so as to negate the spontaneous pressure gradient that was otherwise engendered. He determined the ratio of the magnitudes of both component fluxes and noted the fluxes pointed in opposite directions. In the context of the foregoing equations, Graham measured the magnitude and direction of N_i^D, $i = A, B$, for 10 gas pairs. His experiments foretold Equation 21, a result we have seen to arise from the momentum balance for the gas as a whole under isobaric conditions. We emphasize that Graham's law holds only under the isobaric condition but Equation 19 holds for both variable and constant pressure. Graham's law has been experimentally verified many times (e.g., Evans III et al., 1962; Gunn and King, 1969) since Graham's pioneering investigations.

4.5   Molecular, Knudsen, and Transition Regimes

Resistance to diffusion resulting from both molecule-molecule and molecule-particle collisions is included in Equations 14 and 15 but no hints have yet been offered as to the conditions that dictate their relative importance. A qualitative guide to the relative importance of the resistance terms is provided by the Knudsen number, defined as the ratio of mean free path length to the characteristic pore dimension, $K_n = \lambda/\lambda_p$ The mean free path length, λ, is the average distance traveled by molecules between collisions with other molecules and can be calculated from elementary kinetic theory. The mean free path length is inversely proportional to gas pressure, but the gas pressure in most applications of interest to readers of this book will likely differ little from one atmosphere.

Various measures could be used to characterize pore dimension, but we elect to use the square root of intrinsic permeability, $\lambda_p = k^{0.5}$. This is a natural choice because intrinsic permeability is proportional to the square of a characteristic pore dimension (Freeze and Cherry, 1979; Corey, 1994; Hubbert, 1956) and is determined or estimated in almost any study of fluid movement in the subsurface. Furthermore, it provides an immediate link between the Knudsen number and the range of porous media of interest to the earth scientist.

The terms involving the Knudsen diffusion coefficient in Equations 14 and 15 are negligible for the condition $K_n << 1$. From the point of view of the gas molecules, the diffusion space appears to be densely populated with molecules but only sparsely populated with solid particles for $K_n << 1$. For this condition, molecules are likely to experience a great many intermolecular collisions before encountering a solid particle. Thus, the resistance offered to diffusion of individual components via molecule particle-collisions is negligible relative to that offered by inter-molecular collision (i.e., $D_i^K \gg D$) The diffusion regime is said to be molecular in this case. Note that small resistance to diffusion is characterized by large diffusion coefficients, just as small resistance to viscous flow corresponds to large permeability.

At the other extreme, terms involving the molecular diffusion coefficient are negligible and the Knudsen regime prevails when $K_n \gg 1$. Now it is the particles that densely populate the diffusion space and solid surfaces appear in close proximity to all of the gas molecules as measured relative to the mean free path length. The probability of molecule-particle collisions overwhelms the probability of molecule-molecule collisions and the diffusion is said to be occurring in the Knudsen regime. When neither molecular nor Knudsen diffusion dominates, diffusion occurs in the transition regime.

Suppose nitrogen gas at 20°C and one atmosphere pressure is present in clean coarse sand with an intrinsic permeability of 1×10^{-10} m². For this case, λ is about 6.5×10^{-8} m as calculated from $\lambda = 1/(2^{0.5}\pi\sigma^2\tilde{n})$, where σ is the diameter of the molecule (3.75×10^{-10} m for N_2; Daniels and Alberty, 1962) and $\tilde{n}$ is the number of molecules per unit volume (2.5×10^{25} m^{-3} for the given temperature and pressure). The square root of intrinsic permeability is $\lambda_p = 1 \times 10^{-5}$ m, and the Knudsen number is about 0.0065. Resistance to diffusion offered by molecule-particle collisions is likely negligible in this case and diffusion is said to be molecular diffusion. On the other hand, the Knudsen number would be 6.5 for the same gas present in a glacial till with an intrinsic permeability of 1×10^{-16} m². This situation is likely in the transition regime in which both molecular and Knudsen diffusion is important.

The values of intrinsic permeability vary widely within the large range of materials that may be of interest to the earth scientist. Based on the calculations in the above paragraph, the molecular regime can be expected to prevail in materials with an intrinsic permeability greater than about 1×10^{-12} m². The transition regime is likely to prevail in the remainder of the permeability range of interest to the practicing earth

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scientist. These guidelines are intended to provide the reader only with a rough idea of where the diffusion regimes might occur in the permeability range of interest.

The above discussion might lead one to erroneously conclude that diffusion in the molecular regime is independent of molecule-particle collisions. Even when such collisions are negligible in the context of resistance to diffusion of individual components, molecule-particle collisions remain very important in the context of the momentum balance for the gas as a whole, regardless of the prevailing diffusion regime. Therefore, the coupling between the diffusive fluxes expressed in Equations 20 and 21 must be satisfied in all diffusion regimes because they follow from the momentum balance for the gas as a whole.

5   Flux Equations

With Equation 14 now understood in the context of conservation of momentum, we replace partial pressure, P_A, with the more familiar molar concentration, C_A and use Equation 10 to replace J_A and obtain Equation 22.

$$-D \, dC_A/dl = (x_B N_A^D - x_A N_B^D) + (D/D_A^K)N_A^D \tag{22}$$

Equation 22 and the corresponding equation for species B (interchange the subscripts) apply in both the molecular and transition regimes under both isobaric and non-isobaric conditions. The total diffusive fluxes are expressed by Equations 20 and 21 for the non-isobaric and isobaric condition, respectively.

5.1   Molecular Regime – Uniform Pressure

Resistance to diffusion of an individual species in the molecular regime is dominated by inter-molecular collisions, so the ratio D/D_A^K is very small and the second term on the right side of Equation 22 is negligible. Also, Graham's law and the relation $dC_A = C dx_A$ apply for the isobaric condition. Equation 22 becomes Equation 23.

$$- N_A^D = - \frac{DC \, dx_A/dl}{1 - (1 - M_{AB}^{0.5})x_A} \tag{23}$$

The diffusive flux for species B is obtained from Equation 23 by interchanging the subscripts (note: $M_{BA} \equiv M_B/M_A$.). Strictly speaking, these results become Fick's law only if the molecular weights of the species are the same. However, diffusion is closely approximated by Fick's law when the molecular weights are nearly equal and/or when one species is present in dilute concentration (i.e., $x_A << 1$). The latter situation is common in environmental applications where the species of interest often appears in only trace amounts (e.g., vapor from a neat liquid with low vapor pressure or evaporation from the dissolved state in aqueous solution).

Integration of Equation 23 for steady-state diffusion between open boundaries on which the pressure is the same is demonstrated in subsequent examples. Non-equimolar diffusion results in the development of a pressure gradient in any system in which the free flux of gas components is prevented on one (a semi-open system) or both boundaries

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(a closed system). Even in completely open systems, transient pressure gradients are present during unsteady diffusion (Fen and Abriola, 2004). Thus, the isobaric condition under which Equation 23 applies is expected to occur rarely if ever in natural field settings. The case of simultaneous diffusion and viscous flow is addressed in the following section. Click on these exercise links to view example problems Exercise 1↓ and Exercise 2↓.

5.2   Molecular Regime – Non-uniform Pressure

The total flux of a component is the sum of the total diffusive flux and the advective flux resulting from viscous flow (Equation 3). The advective flux resulting from viscous flow is the product of the mole fraction and viscous flux, as explained previously. Then our task is reduced to determining the total diffusive flux affected by non-uniform pressure. The spadework pertinent to this task has already been accomplished. Neglect the second term on the right side of Equation 22 because we are considering the molecular regime and substitute Equation 20 for N_B^D in the remaining term. Upon rearrangement we have Equation 24.

$$N_A^D = - \frac{DC \, dx_A/dl + (D + D_B^K)x_A \, dC/dl}{1 - (1 - M_{AB}^{0.5})x_A} \tag{24}$$

Equation 24 uses $dC_A = Cdx_A + x_AdC$. When the ideal gas law is used to replace the total molar concentration gradient with the gradient of gas pressure, we see that the second term in this result calculates the effect of pressure gradient on diffusion. This effect is sometimes referred to as pressure diffusion. Recall the discussion in Section 3.0 in which we identified the pressure gradient in the bulk gas as a driving force for diffusion of individual species, as well as for viscous flow.

The flux equation for species *A* (interchange subscripts for species *B*) affected by both diffusion and advection via viscous flow is obtained by simply adding the viscous advective flux to Equation 24. We then have Equation 25.

$$N_A = - \frac{DC \, dx_A/dl + (D + D_B^K)x_A \, dC/dl}{1 - (1 - M_{AB}^{0.5})x_A} - x_A(k_g p/\mu) \, dC/dl \tag{25}$$

This equation is readily reduced to the simpler expression of Equation 26 for the condition $D_B^k \mu / k_g p \ll 1$.

$$N_A = - \frac{DC \, dx_A/dl}{1 - (1 - M_{AB}^{0.5})x_A} - x_A(k_g p/\mu) \, dC/dl \tag{26}$$

This simplification is tantamount to assuming that $dC_A \approx Cdx_A$ (i.e., pressure diffusion is negligible) and that the total diffusion flux is satisfactorily approximated by Equation 23. Note that the product DC is independent of pressure, owing to the fact that the effective diffusion coefficient is inversely proportional to pressure. Click on these exercise links to view example problems Exercise 3↓ and Exercise 4↓.

5.3   Transition Regime – Constant and Non-uniform Pressure

Diffusion in the transition regime is distinguished by the fact that resistance to diffusion offered by both molecule-molecule and molecule-particle collisions must be considered. That is, the second term on the right of Equation 14 must be retained. For the isobaric condition, the relation between the component fluxes is given by Graham's law, Equation 21. Upon introduction of Equation 21 into Equation 22, followed by some algebraic manipulation, the equation for the flux of species A under isobaric conditions is derived to be Equation 27.

$$N_A^D = -\frac{DC\, dx_A/dl}{(1 + D/D_A^k) - (1 - M_{AB}^{0.5})x_A} \qquad (27)$$

The corresponding result for the non-isobaric condition is obtained by using Equation 20 in Equation 22 and adding advection via viscous flow to obtain Equation 28.

$$N_A = -\frac{DC dx_A/dl + (D + D_B^k)x_A dC/dl}{(1 + D/D_A^k) - (1 - M_{AB}^{0.5})x_A} - x_A(k_g P/\mu)\, dC/dl \qquad (28)$$

As usual, the corresponding equation for the flux of species B is obtained by interchanging the subscripts.

We appealed to the conditions $D/D_i^k \ll 1, i = A, B$ and $D_i^k \mu/k_g p \ll 1, i = A, B$ to justify simplifications leading to Equation 26, applicable in the molecular regime. Neither of these conditions generally applies in the transition regime now under consideration. However, important to groundwater scientists and engineers is the circumstance in which the species of interest, say species A, is present only in trace concentrations. Equation 28 can then be simplified to Equation 29.

$$N_A = -\frac{DC dx_A/dl}{(1 + D/D_A^k)} - \left(\frac{D + D_B^K}{1 + D/D_A^K} + k_g p/\mu\right) x_A\, dC/dl \qquad (29)$$

This result is of the same mathematical form as the widely used advection-diffusion model. Webb and Pruess (2003) calculated the transport of trace species using a flux equation that can be derived from Equation 29 written on a mass flux basis. Click on this exercise link to view an example problem [Exercise 5](#)⤵.

5.4   Transition Regime - A Pure Gas

We have seen that the fluxes of individual species in a binary mixture are affected by mole-fraction diffusion, pressure diffusion and viscous flow. Only pressure diffusion and viscous flow occur in a pure gas. The diffusion flux for a single-species gas as shown in Equation 30 follows immediately from Equation 22.

$$N^D = -D^K\, dC/dl \qquad (30)$$

The viscous flux is added to the diffusion flux as usual to obtain the Equation 31 for the mole flux of a pure gas.

$$N = -(D^K + k_g p/\mu)dC/dl \tag{31}$$

Equation 31 shows that the viscous flux calculated by Darcy's law is a satisfactory approximation of the total flux of a single component gas when conditions in the molecular regime satisfy the criterion expressed in Equation 32.

$$\frac{\mu D^K}{k_g P} \ll 1 \tag{32}$$

Klinkenberg (1941), as well as Heid and others (1950), present experimental data for the flux of air in response to pressure gradients in porous media with low permeability where the diffusion contribution is significant. These data and Equation 31 play a key role in the following section wherein we address the estimation of numerical values for the Knudsen diffusion coefficients.

6 Estimation of Diffusion Coefficients

The diffusion coefficients appearing in the above developments are macroscopic parameters. Macroscopic values for these parameters are automatically obtained when measured by application of macroscopic equations. The estimation of Knudsen diffusion coefficients by the method described in this section is an example of this circumstance. On the other hand, values for molecular diffusion coefficients tabulated in handbooks are not macroscopic and must be modified to account for obstructions present in the diffusion space.

6.1 Effective Molecular Diffusion Coefficient

The molecular diffusion coefficient, D_m (L²/T), that appears in Equation 13 applies when the diffusion space is free of obstruction. This is the parameter that has been widely measured and tabulated in handbooks and reference works. Typical values for common gas pairs often fall in the range 1×10^{-5} to 1×10^{-4} m²/s. It can be shown from kinetic theory that diffusion in a particular gas pair is characterized by a single molecular diffusion coefficient (Cunningham and Williams, 1980). Further, for the conditions of interest in this book, the molecular diffusion coefficient is proportional to p^{-1} and $T^{2/3}$ while being practically independent of composition.

The existence of obstructions in the diffusion space causes the effective (macroscopic) molecular diffusion coefficient to be less than the molecular diffusion coefficient applicable in particle-free space. The effective diffusion coefficient must be determined by an appropriate direct measurement for the problem at hand or estimated by suitable adjustments to the free space coefficient, D_m. The effective molecular diffusion coefficient is often calculated from Equation 33.

$$D = \theta_g \tau D_m \tag{33}$$

where:

θ_g = fraction of bulk porous medium that is occupied by gas, i.e., volumetric gas content (dimensionless)

τ = tortuosity (dimensionless)

The volumetric gas content accounts for the reduction of area available for gas diffusion because part of the macroscopic cross-sectional area is occupied by solids and other fluids. The tortuosity adjusts for the fact that the observable macroscopic distance between two macroscopic points is less than the distance along the tortuous pore-scale travel path. The values of both parameters are less than unity.

A popular empirical expression for tortuosity is shown in Equation 34 (Millington and Quirk, 1961).

$$\tau = \theta_g^{7/3}/n^2 \qquad (34)$$

where:

n = porosity (dimensionless)

For a dry porous medium, the volumetric gas content equals porosity and the corresponding tortuosity is $n^{0.33}$. Dry, loose sand with a porosity of 0.35 can be expected to have a tortuosity of about 0.7, according to Equation 34. Notice, however, the tortuosity falls rapidly as the gas content decreases. Furthermore, the volumetric gas content itself is highly sensitive to the heterogeneity of the porous medium. Consequently, the effective diffusion coefficient can be expected to exhibit large, even extreme, spatial variability in field problems. A single fine-grained layer oriented normal to the diffusion path, even if very thin, may effectively block and re-direct gas-phase diffusion because of small gas content.

Calculation of the effective diffusion coefficient by the procedure outlined above (or similar calculation) is popular because it is simple and inexpensive. Field measurements of the effective diffusion coefficient offer an alternative when they can be made with reasonable effort and reliability. Field measurements are accomplished by fitting a suitable diffusion model to appropriate field measurements (e.g., Johnson et al., 1998; Kreamer et al., 1988; Weeks et al., 1982). Values of the effective diffusion coefficient determined in this way are automatically macroscopic values and reflect the effects of spatial variability over some scale.

The method presented by Johnson et al. (1998) is a particularly innovative and practical example of this procedure. A known mass M_0 of inert tracer gas that does not significantly partition into water is mixed with air in a small volume, V_0. This volume is injected at a "point" from which it spreads radially by diffusion. A measured volume V_S of the gas mixture, larger than the injected volume, is subsequently withdrawn (at time t_S) from the point of injection and the mass $M(t_S)$ of extracted tracer gas is determined. The effective diffusion coefficient is calculated from Equation 35.

$$D = \frac{\theta_g^{1/3}}{4t_s\beta}\left(\frac{3V_s}{4\pi}\right)^{2/3} \tag{35}$$

where:

β = a dimensionless parameter

The dimensionless parameter β only depends upon the ratio of recovered to injected tracer mass and is determined from the implicit Equation 36.

$$M(t_s)/M_o = \text{erf}\,(\beta^{1/2}) - 2\left(\frac{\beta}{\pi}\right)^{1/2} exp(-\beta) \tag{36}$$

The volumetric gas content appearing in Equation 35, θ_g, is usually not measured. However, the calculation of D from Equation 35 is not very sensitive to θ_g and a reasonable estimate for θ_g is sufficient in most cases.

Equations 35 and 36 follow from the solution of Fick's law-based partial differential equation for unsteady radial diffusion from a point source. The developments in this book predict that transient non-equimolar and viscous fluxes are engendered by unsteady diffusion from a point source and in many other cases of unsteady diffusion. There exists a paucity of solutions for unsteady diffusion that are based on the flux equations of this book, and it remains unknown whether solutions derived from differential equations based on Fick's law constitute suitable models in the sense used above. However, any differences between effective diffusion coefficients derived by fitting either Fick's law-based models or models based on the flux equations of this book will likely be overwhelmed by the range of uncertainty in the determination, irrespective of which flux equations are used.

6.2   Effective Knudsen Diffusion Coefficient

Equation 31 calculates the mole flux of pure gas subjected to a pressure gradient. The flux of a pure gas is comprised of both diffusive and viscous contributions as indicated by the two coefficients in parentheses. Equation 31 suggests that the effective Knudsen diffusion coefficient can be estimated from measured values of the quantity in parentheses, together with independently determined values for permeability (Thorstenson and Pollock, 1989; Webb, 2006) and that procedure is presented in the following paragraphs.

Klinkenberg (1941) was interested in the estimation of liquid permeability of porous media from measurements made with air. He determined the quantity in parentheses in Equation 31 from measurements of volume flux of air and the corresponding pressure gradient from which he computed an apparent permeability. Thus, Klinkenberg's apparent permeability included a contribution from Knudsen diffusion. The apparent permeability was found to be a function of the mean pressure at which the experiments were conducted. A plot of apparent permeability versus the inverse mean pressure was approximately linear with slope b. The graph was extrapolated to $\bar{P}^{-1} = 0$ to provide a value for the apparent permeability to air at a

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pressure sufficiently large to preclude a contribution by Knudsen diffusion. Because the experiments were conducted with dry porous media, the extrapolated value was taken to be the intrinsic permeability, k, of the porous medium. Klinkenberg's results can be expressed by Equation 37.

$$\frac{k_a \bar{P}}{\mu} = \left(\frac{k \bar{P}}{\mu}\right)\left(1 + \frac{b}{\bar{P}}\right) \tag{37}$$

The left side of Equation 37 contains the measured apparent value of permeability, k_a, and the right side contains the intrinsic value. The parameter b is known as the Klinkenberg parameter. Equation 38 follows from Equation 31 and 37.

$$\frac{D^k \mu}{k} = b \tag{38}$$

Heid et al. (1950) correlated the Klinkenberg parameter with intrinsic permeability from more than 150 measurements over the permeability range 10^{-17} to 10^{-12} m^2 to arrive at Equation 39.

$$b = 0.11(k)^{-0.39} \tag{39}$$

where:

k = permeability (must be in m^2)

b = Klinkenberg parameter (expressed as Pascals)

When permeability is expressed in m^2, Equation 39 returns a Klinkenberg parameter value with units of Pascals (Thorstenson and Pollock, 1989). Equation 39 was developed from measurements with air flow through dry porous media, so values of Knudsen diffusion coefficients computed from Equations 38 and 39 are specific for air in dry media and are given the symbol D_a^K. Coefficients for other gases in dry porous media can be determined from Equation 40.

$$D_i^K = (M_a/M_i)^{0.5} D_a^K \tag{40}$$

The subscripts a and i denote air and the gas of interest, respectively. Equation 40 is Equation 19 rewritten specifically for the case at hand. The procedure is as follows: 1) determine the intrinsic permeability, 2) compute b from Equation 39 and use Equation 38 to compute the Knudsen diffusion coefficient for air, and 3) calculate the Knudsen diffusion coefficient for the gas of interest from Equation 40.

The porous media of interest in field applications are rarely dry. The presence of water in porous media reduces the characteristic dimension of the space available for gas diffusion and, therefore, causes Knudsen diffusion to be more significant than if the medium were dry. Thus, it may be important to estimate values for the Knudsen diffusion coefficients even in rather coarse-grained media. First-cut estimates of Knudsen diffusion coefficients, affected by the presence of water, can be made by using the effective gas permeability, k_g, determined at the water content of interest, in place of the intrinsic permeability k in the above procedure.

Reinecke and Sleep (2002) found that this first-cut approximation overestimated the Knudsen diffusion coefficient for air when compared to experimental measurements. These authors propose the correlation of Equation 41.

$$D_a^K = 2.69 \times 10^6 \left(k_g\right)^{0.764} \tag{41}$$

Equation 41 yields the Knudsen diffusion coefficient for air in cm²/s corresponding to an effective gas permeability expressed in cm². The values for other gases follow from Equation 40.

The above procedure offers a practical way to estimate the difficult to measure Knudsen diffusion coefficients that are required for the application of the flux equations developed in the foregoing paragraphs. Note that the values of Knudsen diffusion coefficients calculated from the above procedure are already effective (macroscopic) values and do not require adjustments for tortuosity and open area.

7   Summary and Conclusions

The molecules of gases exist in a state of continuous random, chaotic motion. In multi-component gases with non-uniform composition, individual components spontaneously diffuse from locations of high to low concentrations because the component energy per unit volume is greater at high concentration than at low concentration. Diffusing molecules in systems free of solid particles experience a resistance to their collective motion due to collisions with molecules of other components. The rate at which there occurs a net transfer of component molecules from one location to another is represented by Fick's law and is characterized by the molecular diffusion coefficient.

Gases diffusing through porous media experience an additional resistance to motion caused by the collision of molecules with solid particles embedded in the gas. The effect of molecule-solid collisions on the rate of diffusion is characterized by the effective Knudsen diffusion coefficient. When the diffusion problem of interest occurs in the transition regime (porous solids of small to moderate permeability), the applicable flux equations involve both the molecular and Knudsen diffusion coefficients. This is because neither inter-molecular nor molecule-solid collisions dominate in the transition regime. These flux equations will appear unfamiliar to those who are used to thinking about diffusion in spaces free of obstruction where Fick's law applies.

The molecular diffusion regime prevails when the pores are so large that molecule-molecule collisions account for essentially all resistance to diffusion. This regime occurs in porous media with moderate to high permeability. Even in this case, diffusion fluxes are not independent of molecule-solid collisions and the component flux equations are generally not the familiar Fick's law expressions. Molecule-solid collisions during isobaric diffusion in the molecular diffusion regime are responsible for the fact

that component fluxes are not of equal magnitude. The difference between the magnitudes of the fluxes is a diffusion-generated bulk flow that is not a viscous flow (i.e., there is no pressure gradient associated with this non-equimolar flow). This case becomes a familiar Fick's law problem if the molecular weights of the diffusing species are equal or if the species of interest is present only in trace quantities (i.e., mole fraction of one component everywhere is much less that unity). The latter of these conditions is often encountered in environmental applications.

Isobaric diffusion can be established in the laboratory where the pressure on the system boundaries can be externally controlled, but diffusion-generated viscous flow and associated pressure gradients are to be expected in virtually all field settings. We have provided an example of how this occurs in a semi-open system at steady state. Even in a completely open system, transient pressure gradients develop during unsteady flow. However, the practical significance of diffusion-generated pressure gradients is a separate question, one for which an answer can be provided only on a case-by-case basis.

8   Exercises

Exercise 1

Argon and helium diffuse through dry fine sand with a porosity $n = 0.3$ in the diffusion chamber of Figure Exercise 1-1. The molecular weights are 39.9 g/mole for argon (species *A*) and 4 g/mole for helium (species *B*). The pressure in both headers is maintained at 1×10^5 Pa and the temperature is 25 °C. The effective molecular diffusion coefficient is 2.37×10^{-5} m²/s under these conditions. To a close approximation, the mole fraction of argon is $x_A = 1$ in the left header and $x_A = 0$ in the right header. The diffusion chamber is 0.05 m long. For the steady-state condition:

a) Compute the magnitude and direction of the total diffusive mole flux for both species. Compare with the values of flux computed from Equation 11.

b) Compute the magnitude and direction of the non-equimolar flux.

c) Derive an equation for $x_A(l)$ that shows how x_A varies along the diffusion path.

d) Compute the values for J_A and J_B at the midpoint of the diffusion chamber.
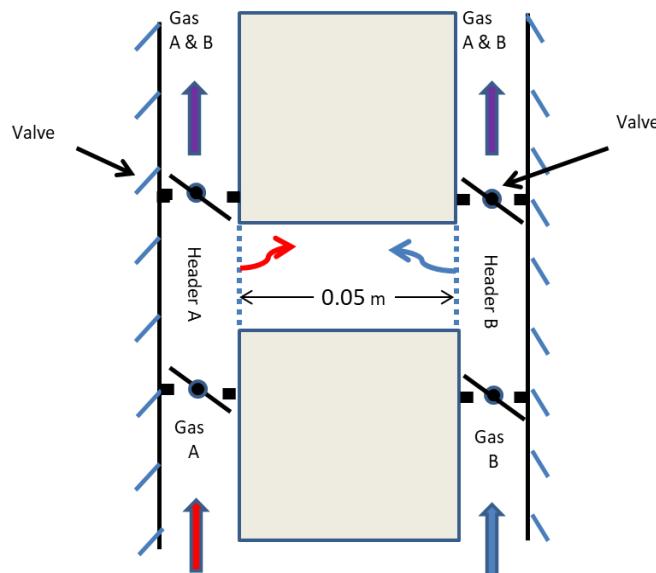
Figure Exercise 1-1 - Isobaric diffusion of argon (species A) and helium in a sand-filled chamber.

Exercise 2

Flux equations such as Equation 23 are often referred to as constitutive equations. Darcy's law and Fick's law are familiar examples. Derive the constitutive equation for the non-equimolar flux for isobaric diffusion in the molecular regime.

Exercise 3

Consider again the diffusion of argon and helium as described in Exercise 1. All conditions are the same in the present problem except that the pressure in the left-hand header is elevated just enough to cause the steady-state mole fluxes of argon and helium to be equal in magnitude and opposite in direction. Assume that diffusion due to the pressure gradient is negligible. If the intrinsic permeability of the dry sand is 1×10^{-12} m^2 and the viscosity of the gas is 2.3×10^{-5} Pa-s, calculate the pressure difference between the headers.

Click here for solution to Exercise 3

Click here to return to where the text links Exercise 3

Exercise 4

Aerobic biodegradation of petroleum hydrocarbons present in the vadose zone is manifest by a predominately upward flux of carbon dioxide. The magnitude of CO_2 flux is an indicator of the rate of depletion of the liquid-phase hydrocarbon. Among the various methods that have been used to estimate the CO_2 flux in the field is the so-called gradient method, by which the upward flux is computed from a measured concentration distribution and the effective diffusion coefficient. More than two gas components are involved in the depletion of a liquid-phase hydrocarbon by aerobic biodegradation. Nevertheless, it is instructive to revise the gradient method using the flux equations for a binary gas in which air and carbon dioxide are assumed to be the only two constituents.

Refer to Figure Exercise 4-1 and derive an equation by which the steady CO_2 flux can be calculated from a measured concentration distribution and a known effective diffusion coefficient. Assume the molecular regime prevails, pressure diffusion is negligible, and air can be considered to be a single species (species *A*).

Compute the mole flux of carbon dioxide, phase (bulk gas) flux, non-equimolar flux, and viscous flux using the following data from Tracy (2015).

$$p = 8.3 \ x \ 10^4 \ Pa$$
$$T = 21.6 \,°C$$
$$D = 4.7 \ x10^{-6} \ m^2/s$$
$$z_2 - z_1 = 1.29 \ m$$
$$x_B(z_1) = \ 0.0583$$
$$x_B(z_2) = 0.0013$$
$$M_{BA}^{0.5} = 1.232$$
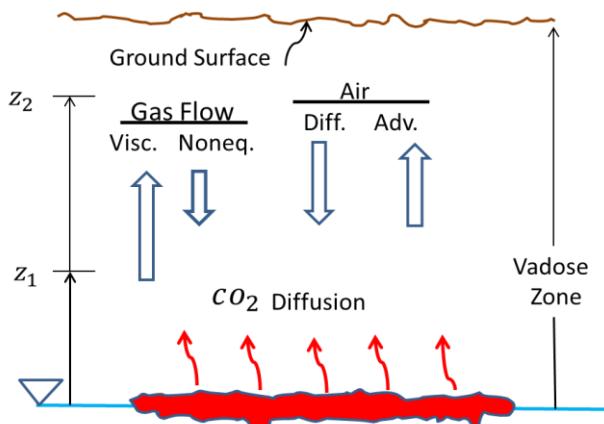
**Figure Exercise 4-1 -** Sketch of steady diffusion of carbon dioxide in the vadose zone from a source at the water table.

Exercise 5

Use Equation 27 to demonstrate that Graham's law of diffusion holds for isobaric diffusion in the transition regime.

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10   Exercise Solutions

Exercise 1 Solution

Part a)

Arbitrarily set the origin of the coordinate, l, at the left end of the diffusion chamber. The value of l on the right-hand end of the chamber is L, equal to 0.05 m. Equation 23 is applicable because diffusion occurs in the molecular regime with no pressure gradient. At steady state, the total diffusive flux of each component is constant with respect to time and position along the diffusion path. Thus, Equation 23 is integrated to obtain Equation Exercise Solution 1-1.

$$N_A^D = \frac{DC}{(1-M_{AB}^{0.5})L} \, ln\left\{\frac{1-(1-M_{AB}^{0.5})x_A(L)}{1-(1-M_{AB}^{0.5})x_A(0)}\right\} \qquad \text{(Exercise Solution 1-1)}$$

where:

$x_A(L)$ = mole fraction of argon at $l = L$

$x_A(0)$ = mole fraction of argon at $l = 0$

The molar concentration is computed from the ideal gas law, $C = P/RT$,

with: $P = 1 \times 10^5 \, Pa$, $R = 8.205 \frac{m^3 \, Pa}{deg-mole}$ and $T = 298 \, K$.

$$C = \frac{P}{RT} = \frac{10^5 \, Pa}{8.205 \frac{m^3 \, Pa}{deg \ mole} 298 \, K} = 40.9 \frac{moles}{m^3}$$

Other parameter values are:

$x_A(L) = 0, x_A(0) = 1, M_{AB}^{0.5} = 3.158, L = 0.05 \, m$ and $D = 2.37 \times 10^{-5}$ m²s⁻¹.

The total diffusive flux of argon is:

$$N_A^D = \frac{(2.37 \ x \ 10^{-5})(40.9)\{ln(3.158^{-1})\}}{(1-3.158)(0.05)} = 0.0103 \frac{moles}{m^2 \ s}$$

The flux of argon is positive because it is in the direction of increasing l.

The flux of helium can be calculated from Equation Exercise Solution 1-1 after interchanging the subscripts. However, the flux of helium is computed more easily from Graham's law:

$$N_B^D = -M_{AB}^{0.5} \, N_A^D = -3.158 \, (0.0103) = -0.0325 \frac{moles}{m^2 \ s}$$

The corresponding values of flux computed from Fick's law (Equation 11) are 0.019 moles/(m²s) for species A and -0.019 moles/(m²s) for species B. The Fick's law calculation results in a rather large error in this case as there is significant disparity between the molecular weights of the gas components.

Part b)

The non-equimolar flux or net flux is given by Equation 5.

$$N^D = N_A^D + N_B^D = 0.0103 - 0.0325 = -0.0222 \frac{moles}{m^2 \, s}$$

This is the flux of the gas as a whole. It is engendered entirely by diffusion, occurs without loss of momentum by viscous shear, and is in the direction of diffusion of the lighter component (helium).

Part c)

Integrate Equation 23 subject to $x_A = x_A(l)$ at position l and $x_A = 1$ at $l = 0$ or use Equation Exercise Solution 1-1 to obtain Exercise Solution 1-2.

$$N_A^D = \frac{DC}{(1 - M_{AB}^{0.5})l} \ln \left\{ \frac{1 - (1 - M_{AB}^{0.5})x_A(l)}{M_{AB}^{0.5}} \right\} \qquad \text{(Exercise Solution 1-2)}$$

However, $x_A(L) = 0$, consequently, Equation Exercise Solution 1-2 becomes Equation Exercise Solution 1-3.

$$N_A^D = \frac{DC}{(1 - M_{AB}^{0.5})L} \ln \left(\frac{1}{M_{AB}^{0.5}} \right) \qquad \text{(Exercise Solution 1-3)}$$

The desired result is obtained by combining these two equations and solving for $x_A(l)$ to obtain Exercise Solution 1-4.

$$x_A(l) = \frac{1 - exp\{(1 - l/L)\ln M_{AB}^{0.5}\}}{1 - M_{AB}^{0.5}} \qquad \text{(Exercise Solution 1-4)}$$

Part d)

Equation 10 is combined with Graham's law to obtain Exercise Solution 1-5.

$$J_A = N_A^D \{1 - x_A(1 - M_{AB}^{0.5})\} \qquad \text{(Exercise Solution 1-5)}$$

Then Equation Exercise Solution 1-4 is substituted for x_A to arrive at Equation Exercise Solution 1-6.

$$J_A(l) = N_A^D exp\{(1 - l/L)\ln M_{AB}^{0.5}\} \qquad \text{(Exercise Solution 1-6)}$$

Equation Exercise Solution 1-6 shows how the equimolar flux varies over the length of the diffusion chamber.

At a point midway between the supply headers ($l/L = 0.5$), we have

$$J_A = (0.0103) \, exp\{0.5 \ln(3.158)\} = 0.0183 \frac{moles}{m^2 \, s}$$

The corresponding helium flux follows from Equation Exercise Solution 1-6 by interchanging the subscripts to obtain:

$$J_B = (-0.0325)exp\{0.5ln(0.317)\} = -0.0183 \frac{\text{moles}}{m^2\ s}$$

These molar fluxes are equal in magnitude and opposite in direction so they satisfy Equation 7. This numerical computation applies to a particular point, and we leave it to the reader to demonstrate that Equation Exercise Solution 1-6 and its counterpart for component *B* sum to zero at all points. Of course, this must be the case because Equation 7 is at the heart of the analysis leading to the starting point for this example, Equation 23.

Exercise 2 Solution

Start with Equation 5, which defines the non-equimolar flux.

$$N^D \equiv N_A^D + N_B^D = \left(1 + N_B^D/N_A^D\right)N_A^D$$

Use Graham's Law to obtain the following expression.

$$N^D = \left(1 - M_{AB}^{0.5}\right)N_A^D$$

Then replace the total diffusion flux of component *A* using Equation 23 to obtain the desired constitutive equation (Equation Exercise Solution 2-1).

$$N^D = -\frac{\left(1-M_{AB}^{0.5}\right)DCdx_A/dl}{1-\left(1-M_{AB}^{0.5}\right)x_A} = -\frac{\left(1-M_{BA}^{0.5}\right)DCdx_B/dl}{1-\left(1-M_{BA}^{0.5}\right)x_B} \qquad \text{(Exercise Solution 2-1)}$$

Underpinning this development is the prescription of uniform pressure. However, Section 5.2 illustrates that Equation Exercise Solution 2-1 is a satisfactory approximation under non-isobaric conditions when diffusion that is driven by variable pressure is negligible relative to that driven by gradients of mole fraction.

Exercise 3 Solution

From Equation 8c, the condition $N_A + N_B = 0$ requires that the viscous flux cancel the non-equimolar flux: $N^v = -N^D$.

The value of the non-equimolar flux ($N^D = -0.0222 \frac{\text{moles}}{m^2\,s}$) computed in Exercise 1 applies here because the diffusive fluxes are not appreciably affected by the pressure gradient. So $N^V = 0.0222 \frac{\text{moles}}{m^2\,s}$ and, from Equation 2, $N^v = -\frac{k_g}{\mu RT} p\, dp/dl = 0.0222 \frac{\text{moles}}{m^2\,s}$.

This is integrated to obtain the following expression

$$\frac{k_g}{2\mu RTL}\left(p_0^2 - p_L^2\right) = 0.0222$$

which can be used to directly calculate the desired pressure difference. However, computations are facilitated by rewriting the left side using:

$$\frac{1}{2}\left(p_0^2 - p_L^2\right) = \bar{p}(p_0 - p_L)$$

where, $\bar{p}$ is the average pressure in the chamber.

$$p_0 - p_L = 0.0222\, \frac{\mu L}{Ck_g} = \frac{(0.0222)\left(2.3\, x\, 10^{-5}\right)(0.05)}{(1\, x\, 10^{-12})(40.9)} = 624\, Pa$$

The pressure drop is quite small (about *6 cm H2O*) relative to the 1×10^5 Pa pressure maintained in the right-hand header, justifying the assumption that the mean pressure is closely approximated by the controlled pressure in the right-hand header.

Return to Exercise 3⤴

Exercise 4 Solution

Part a)

The water table constitutes a zero-flux boundary for both air and carbon dioxide. The air flux must be zero everywhere because the flux is zero at the boundary, there are no sources or sinks for air, and the system is at steady state. On the other hand, carbon dioxide is generated by an aerobic source present near the base of the vadose zone. The carbon dioxide migrates upward toward the ground surface at a steady rate.

A qualitative understanding of this problem is described by the following reasoning. Because the source is at the base, the concentration of carbon dioxide must decrease in the upward direction. It follows that the concentration of air must decrease in the downward direction and, therefore, air must diffuse downward from the surface toward the base of the vadose zone in response to the gradient of mole fraction. The rate of downward diffusion of air must be canceled by upward advection in the bulk gas; otherwise, the air would not be stagnant. The concentration gradient drives upward migration of carbon dioxide, enhanced by upward advection. The motion of the gas as a whole (phase motion) is the sum of the non-equimolar flux and the viscous flux. The non-equimolar flux is directed downward because it always occurs in the direction of diffusion of the constituent with the smaller molecular weight (air in the present case).

Writing Equation 4 with air (species *A*) and with CO_2 (species *B*) results in the following expression.

$$N_A + N_B = N^D + N^v$$

The air is assumed to be stagnant so, $N_A = 0$, which leads to Equation Exercise Solution 4-1.

$$N_B = N^D + N^v \qquad \text{(Exercise Solution 4-1)}$$

The CO_2 flux accounts for the motion of the fluid as a whole (i.e., the phase motion). It is comprised of a non-equimolar flux and a viscous flux.

Writing Equation 26 for the stagnant air component ($N_A = 0$) and combining it with Equation 2 results in Equation Exercise Solution 4-2 for the viscous flux.

$$N^v = \frac{DC \, dx_A/dl}{x_A\{1 - (1 - M_{AB}^{0.5})x_A\}} \qquad \text{(Exercise Solution 4-2)}$$

This expression is used for the viscous flux in Equation 26, written for the carbon dioxide, to obtain Equation Exercise Solution 4-3.

$$N_B = -\frac{DC dx_B/dl}{1-(1-M_{BA}^{0.5})x_B} + \frac{x_B DC dx_A/dl}{x_A\{1-(1-M_{AB}^{0.5})x_A\}} \qquad \text{(Exercise Solution 4-3)}$$

This result is simplified with $x_A + x_B = 1$ and $M_{BA}^{0.5} = M_{AB}^{-0.5}$ to obtain the differential equation shown as Equation Exercise Solution 4-4.

$$N_B = \frac{DC dx_A/dl}{x_A} = -\frac{DC dx_B/dl}{1-x_B} \qquad \text{(Exercise Solution 4-4)}$$

The flux of carbon dioxide is constant (because the system is at steady state), so integration between the points z_1 and z_2, where the mole fractions of CO_2 are $x_B(z_1)$ and $x_B(z_2)$, respectively, provides the equation we seek, Equation Exercise Solution 4-5.

$$N_B = \frac{DC}{z_2 - z_1} \ln \left\{ \frac{1 - x_B(z_2)}{1 - x_B(z_1)} \right\} \qquad \text{(Exercise Solution 4-5)}$$

Equation Exercise Solution 4-4 reduces to Fick's law when one species is present in trace concentrations (e.g., $x_B << 1$). Indeed, it is common practice to employ Fick's law for the estimation of flux by the so-called gradient method (e.g., Tracy, 2015; Johnson et al., 2006; Maier and Schaak-Kirchner, 2014). Such practice is satisfactory if CO_2 is present in only trace quantity, but masks the fact that non-equimolar and viscous fluxes significantly affect the transport, as demonstrated in the following computations.

Part b)

Exercise Solution 4-5 produces a value for N_B.

$C = p/RT =$

$$\text{Numerical evaluation of Equation} \frac{8.3 \times 10^4}{(8.205)(294.6)} = 34.34 \frac{moles}{m^3}$$

$$N_B = \frac{(4.7 \times 10^{-6})(34.34)}{1.29} \ln \frac{(1 - 0.0013)}{(1 - 0.0583)} = 7.5 \times 10^{-6} \frac{moles}{m^2 \, s}$$

With the flux of carbon dioxide known, the phase (bulk gas) flux is as follows.

$$N = N_A + N_B = N_B = 7.5 \times 10^{-6} \frac{moles}{m^2 \, s}$$

For the conditions set out in this example (i.e., negligible pressure diffusion), the non-equimolar flux is given by (Exercise 2).

$$N^D = -\frac{(1 - M_{BA}^{0.5})DC \, dx_B/dl}{1 - (1 - M_{BA}^{0.5})x_B}$$

This is integrated to obtain the following expression.

$$N^D = \frac{DC}{z_2 - z_1} \ln \left[\frac{1 - (1 - M_{BA}^{0.5})x_B(z_2)}{1 - (1 - M_{BA}^{0.5})x_B(z_1)} \right]$$

This is evaluated with the data provided to obtain a value for N^D.

$$N^D = -1.7 \times 10^{-6} \frac{moles}{m^2 \, s}$$

The viscous flux is then calculated.

$$N^v = N_B - N^D = 7.5 \times 10^{-6} - (-1.7 \times 10^{-6}) = 9.2 \times 10^{-6} \frac{moles}{m^2 \, s}$$

We have the remarkable result that the viscous flux exceeds the magnitude of the total mole flux of CO_2. Even though the viscous flux is the dominant flux, the associated pressure gradient can be expected to be quite small provided that the intrinsic permeability is sufficiently large to assure the molecular diffusion regime prevails.

Exercise 5 Solution

Start with Equation 27 for species *B*.

$$N_B^D = - \frac{DC\frac{dx_B}{dl}}{\left(1 + \frac{D}{D_B^k}\right) - \left(1 - M_{BA}^{0.5}\right)x_B}$$

Then, because $x_A + x_B = 1$ and $M_{BA}^{0.5} = M_{AB}^{-0.5}$, the denominator is written as follows.

$$\frac{D}{D_B^k} + 1 - \left(1 - M_{BA}^{0.5}\right)x_B = \frac{D}{D_B^k} + \left\{1 - \left(1 - M_{AB}^{0.5}\right)x_A\right\} M_{AB}^{-0.5}$$

With $\frac{D}{D_B^k} M_{AB}^{0.5} = \frac{D}{D_A^k}$ from Equation 19, the flux of species *B* is shown below.

$$N_B^D = \frac{M_{AB}^{0.5} DC \frac{dx_A}{dl}}{\frac{D}{D_A^k} + 1 - \left(1 - M_{AB}^{0.5}\right)x_A}$$

This combines with Equation 27 to form Graham's law.

$$N_B^D = -(M_{AB})^{0.5} N_A^D$$

11   Notation

Subscript denoting species A	A
Subscript denoting species B	B
Klinkenberg parameter (F/L^2)	b
Moles of gas per unit volume (moles/L^3)	C
Moles of species i per unit volume (moles/L^3)	C_i
Effective molecular diffusion coefficient (L^2/T)	D
Molecular diffusion coefficient (L^2/T)	D_m
Knudsen diffusion coefficient for species i (L^2/T)	D_i^K
Equimolar flux of species i (moles/L^{2}T)	J_i
Intrinsic permeability (L^2)	k
Permeability to gas or effective gas permeability (L^2)	k_g
Apparent gas permeability (L^2)	k_{ga}
Knudsen number	K_n
Coordinate tangent to path of motion (L)	l
Ratio M_A/M_B	M_{AB}
Ratio M_B/M_A	M_{BA}
Molecular weight of specie i	M_i
Molecular mass of specie i	m_i
Porosity	n
Number of molecules per unit volume (L^{-3})	$\tilde{n}$
Mole flux of species i (moles/L^{2}T)	N_i
Mole flux of species i due to diffusion (moles/L^{2}T)	N_i^D
Diffusive flux for the gas as a whole (non-equimolar flux) (moles/L^{2}T)	N^D
Mole flux of gas due to viscous flow (moles/L^{2}T)	N^v
Mole flux of species i due to advection in viscous flow (moles/L^{2}T)	N_i^v
Pressure (F/L^2)	p
Mean pressure (F/L^2)	$\bar{p}$
Partial pressure of species i	p_i
Ideal gas law constant (FL)/(moles temperature)	R
Absolute temperature	T
Volume flux (L/T)	v
Mean speed of species i molecules (L/T)	$\bar{v}_i$
Mole fraction of species i	x_i
Vertical coordinate (L)	z
Volume of gas per unit bulk volume	θ_g
Mean free path length (L)	λ
Characteristic pore dimension (L)	λ_p

Molecular diameter (L) σ

Dynamic viscosity (FT/L^2) μ

Tortuosity τ

About the Author
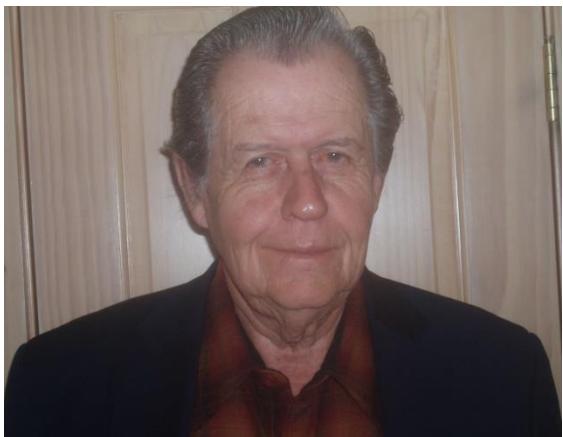
Dr. David B. McWhorter is Professor Emeritus of Chemical and Biological Engineering at Colorado State University. His primary professional interest was the flow of fluids in unsaturated porous media as applied to problems in agriculture, mining, waste disposal, and subsurface contamination. He is author and co-author of numerous research papers and book chapters on these subjects and is co-author with Daniel K. Sunada of the textbook Groundwater Hydrology and Hydraulics. He has received national and university recognition for his teaching and research, including the 2001 M. King Hubbard Award.

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