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Transport by Advection and Diffusion Revisited

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ABSTRACT

Mass transport by advection and diffusion is involved in nearly all branches of science, but various scientific disciplines define the two mechanisms of transport differently. Models widely accepted for combining transport resulting from advection and diffusion are shown to be inconsistent with experimental observations. Experimental observations are cited to show that the barycentric velocity of a solution is not synonymous with velocity as determined by the Navier-Stokes equation of fluid motion. The physics of advection and diffusion is analyzed, and requirements for combining advection and diffusion are presented. Advection is defined here as transport responding to a pressure gradient or body force. Molecular diffusion is defined as transport responding to concentration or thermal gradients. Diffusion represents an average velocity component of molecules of a particular constituent relative to a fixed frame of reference external to the solution, rather than to the mean velocity of all constituents in a solution as defined in current literature. Advection and diffusion contribute independently to the total transport.

A MODEL is proposed for evaluating transport by advection and molecular diffusion that is consistent with experimental observations. Diffusion refers to transport resulting from molecular motion in contrast to *dispersion* resulting from advective velocity gradients. Dispersion is sometimes referred to as *diffusion*, but dispersion refers to a mixing process resulting from turbulence in open bodies of water, or velocity gradients due to heterogeneity in porous materials. Transport of solution constituents by diffusion has applications in many scientific fields.

Evaluating transport by a combination of advection and diffusion has important applications in biology because it is relevant to transport of water and chemicals across cell membranes. Chemical engineers employ a model for combining advection and diffusion in the design of chemical reactors and systems for removing salts from water by reverse osmosis. Transport through compacted clay is an important concern for civil engineers engaged in designing clay barriers for hazardous waste containment. Soil scientists are interested in the movement of aqueous solutions and gases within the plant-soil environment. Combining advection and diffusion is essential for any application involving transport of fluids through porous solids with very small channels.

Two models for evaluating net transport of a constituent in a soil water solution appear in the literature, although there are numerous variations of each. The first model often employed by soil and plant scientists is called the *total potential model*, and the second model, described in textbooks dealing with transport phenomena and non-equilibrium thermodynamics, is referred to here as the *Bird et al. model*.

The total potential approach assumes that the net transport of solution constituents can be calculated in response to a total potential gradient that sums the contributions of component potentials such as pressure, gravitational, concentration, and temperature. Corey and Kemper (1961) presented experimental evidence inconsistent with the total potential assumption. Corey and Klute (1985) provided additional theoretical reasons why the total potential concept fails, and also provided a historical review of the development of the total potential concept.

Briefly, the authors cited showed that resistances to transport in response to gradients of dissimilar potentials are different functions of medium geometry. Although gradients of thermodynamic potentials may describe driving forces, they cannot evaluate resistance forces that also affect the direction and magnitude of net transport. The remainder of this paper deals with models that evaluate net transport as the sum of advection and diffusion.

The best-known model, evaluating net transport as the sum of diffusion and advection, is named after a very popular textbook by Bird et al. (2002). Other textbooks, including those dealing with nonequilibrium thermodynamics, and the authors of many recent papers, describe the same or closely related models. A revised model is suggested in this paper that retains one important feature of the total potential model in that concentration and temperature gradients, as well as pressure gradients and gravity, are assumed to contribute independently to the net transport of solution constituents. A concentration gradient contributes to the average velocity of all constituents, as well as velocity of a particular constituent. *Average velocity* is used here to designate the resultant velocity of individual molecules averaged in a differential cross section of solution in a plane perpendicular to the resultant velocity. Bird et al. (2002) call average velocity defined in this way *local velocity*. Bird et al. (2002) use the term *flux* to denote mass or molar transport averaged in a macroscopic cross section of flow. We use flux also for transport in soils or other porous media, where velocity is averaged in a cross section of porous media.

Models appearing in many modern textbooks, including the text by Bird et al. (2002), depend on two unverified assumptions: (i) Fick's law evaluates the flux of a solution constituent relative to the *mean flux* of all constituents, and (ii) Stokes equation evaluates the mean mass average velocity where Eq. [1] defines mass average velocity.

An objective of this presentation is to show that neither of these assumptions is valid. Equation [6], which

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appears under the heading Revised Model, summarizes our model. We suspect there may be many more scientists who accept a model similar to the one we suggest. However, we have not found published literature pointing out the inconsistency between the Bird et al. model and Eq. [6].

The revised model is not presented as a model for all mechanisms of transport. It is expected to apply only for cases where the driving forces are limited to a body force, pressure gradient, and a kinetic energy gradient resulting from a concentration or temperature gradient. The revised model is not sufficient for the analysis of transport of constituents subject to electrokinetic effects. Electrical forces are important factors in the transport of ions through porous media. However, forces on charged particles do not act evenly on all constituents of a solution and are not proportional to the mass of a reference element of the solution. Consequently, electrical forces cannot be treated as an additional body force, and a rigorous analysis of transport subject to electrical forces on ions is beyond the scope of this presentation.

THE BIRD ET AL. MODEL

The Bird et al. model is described in the textbook *Transport Phenomena*, the first edition of which was copyrighted in 1960, and a second edition was copyrighted in 2002. An identical model is presented in texts dealing with irreversible thermodynamics, such as Haase (1969) and de Groot and Mazur (1984). Bird et al. (2002) view diffusion as a mixing mechanism that does not affect the mass average flux of the solution as a whole. The summation of diffusion fluxes of individual constituents is considered to be zero. Consequently, diffusion as defined for the Bird et al. model does not apply to a solution consisting of a single molecular species.

Bird et al. (2002) define local velocity as a resultant mass velocity averaged in a cross section in a differential reference volume of solution. Reference elements, representing the smallest volumes having a representative density and composition at points in the solution, are called *fluid particles* in fluid dynamics literature. Bird et al. (2002) define *mean velocity* as

$$\boldsymbol{v} = \sum_{1}^{n} (\rho_i/\rho)\, \boldsymbol{v}_i. \qquad [1]$$

They state that Eq. [1] defines the velocity vector appearing in the Stokes equation of fluid motion. The vector $\boldsymbol{v}$ is interpreted as the *mean velocity*, or local mass average velocity, of all constituents in the solution as a whole; ρ is mass per volume of solution; and the subscript $\boldsymbol{i}$ refers to a particular constituent. The term *mean velocity* sometimes is defined by different averaging methods in other literature.

Mass diffusion flux of a constituent in a solution, according to the Bird et al. model, is defined as

$$\boldsymbol{j}_i = \rho_i(\boldsymbol{v}_i - \boldsymbol{v}). \qquad [2]$$

Equation [2] requires that diffusion fluxes sum to zero.

Bird et al. (2002) interpret Fick's law for mass diffusion flux of a constituent as

$$\boldsymbol{j}_i = -\rho\mathfrak{D}_i\nabla(\rho_i/\rho), \qquad [3]$$

where $\mathfrak{D}$ is a diffusion coefficient. Molar diffusion flux of a constituent relative to the molar average velocity is evaluated by

$$\boldsymbol{j}_i^* = -c\mathfrak{D}_i\nabla(c_i/c), \qquad [4]$$

where c is molar concentration.

The text by Bird et al. (2002), as well as irreversible thermodynamic texts (e.g., de Groot and Mazur, 1984), state that $\boldsymbol{v}$ is given by the Navier-Stokes equation of fluid motion, derived by applying Newton's second law of motion to a *fluid particle*. For a fluid continuum undergoing negligible tangential acceleration, and subjected to negligible force due to divergence, the applicable equation is given by

$$\rho\boldsymbol{g} - \nabla p + \mu\nabla^2\boldsymbol{v} = 0. \qquad [5]$$

Equation [5] is called the Stokes flow equation, in which p is pressure; μ is solution viscosity, and $\boldsymbol{g}$ is a body force, usually gravity.

All forces in Eq. [5] have the dimensions of force per volume. However, the gravitational force is a vector acting through the center of mass of a fluid particle, whereas the pressure gradient and viscous shear terms are vectors acting through the centroid of a fluid particle. Consequently, Eq. [5] is strictly rigorous only for homogeneous fluids for which the center of mass and the centroid of fluid particles coincide.

Conceptual Problems with the Bird et al. Model

The velocity vector defined by Eq. [1] is the correct velocity to evaluate the momentum of a moving reference volume (of a homogeneous mixture of constituents) with varying molecular masses. However, the Stokes equation accounts for resistance to fluid rotation only, because tangential acceleration is negligible where advective flux is small and diffusion is a significant mechanism of transport. Fluid rotation results in normal acceleration and viscous shear. Viscous shear is proportional to the rate of angular deformation and is related to volume flux, not *mass average velocity*. Increasing the number of molecules or the mass of species molecules per volume of solution does not increase solution viscosity. In the remainder of this paper, $\boldsymbol{v}$ is used to designate a volume average velocity rather than mass average velocity, although the error resulting from the use of mass average velocity may be small in most cases.

Another conceptual problem is that Bird et al. (2002) relate diffusion to a mass or mole fraction rather than concentration gradient as specified by Fick's law. Fick's law has been verified experimentally many times. We know of no experimental evidence, or theory, supporting constitutive equations relating difusion to a gradient of mole or mass fraction, except in cases for which a mass or mole fraction is a scalar multiple of concentration. For diffusion in incompressible fluids, a concentration gradient may not be significantly different in magnitude from the mole fraction gradient, but for gases subject to a pressure gradient the error is proportional to the pressure gradient.

A more significant problem is that Bird et al. (2002) state that Fick's equation evaluates diffusion as a flux "measured with respect to the motion of the center of mass." Since Fick's law equates diffusion to a gradient relative to external coordinates, we find no reason to suppose that Fick's law evaluates a flux relative to a moving frame of reference. The fact that a flux relative to a solid boundary also contributes to the mean flux does not justify the assumption that the flux evaluated is relative to the mean flux. To demonstrate our reasoning, we suggest the following analogy:

Consider a man walking on a level escalator in an airport. To calculate the velocity of the man relative to external coordinates, one must add the velocity of the man (relative to the escalator) to the velocity of the escalator. One would not add the velocity of the man to the mean velocity of man and escalator. Moreover, it is necessary to evaluate the velocity of the man to determine the mean velocity. Even if Bird et al. (2002) were correct in their assumption that Stokes' equation evaluates the mean velocity, adding a velocity calculated from Fick's law to the mean velocity would not give the velocity of a constituent.

The Bird et al. model assumes that density and temperature gradients have no effect on the mass average velocity of all constituents in a solution, only on the velocity of particular molecular species relative to the mean velocity. Consequently, the Bird et al. model employs Eq. [5] to evaluate mean velocity. Haase (1969) and de Groot and Mazur (1984) refer to $\rho\boldsymbol{v}$ as barycentric velocity, meaning the velocity of the center of mass of a fluid particle. They state that barycentric velocity is evaluated by the Navier-Stokes equation of fluid motion. Evidently, the latter authors also assume that gradients of concentration and temperature are accounted for in the pressure gradient and have no independent effect on barycentric velocity. However, experimental observations show clearly that density and temperature gradients do have an effect on $\boldsymbol{v}$, except for a special case of interdiffusion of molecular species with identical molecular masses under isothermal and isobaric conditions.

Experimental Observations

Evidence contradicting the Bird et al. (1960) model is deducible from published experimental observations. Graham (1833) earlier had published experimental evidence contradicting the Bird et al. (1960) conception of diffusion. Graham's experiments demonstrated that when two molecular species with different molecular masses are interdiffusing in a horizontal system under isothermal and isobaric conditions, significant mean molar and mass average velocities occur in opposite directions. That observation cannot be reconciled with the Bird et al. model for calculating barycentric velocity (Auvermann, 1996.)

Kemper and Rollins (1966) investigated osmotic pressures in soils. They observed that a mean flux, counter to the resultant of a pressure gradient and body force, occurs in porous materials that restrict motion of solute molecules to a greater extent than solvent molecules. The Bird et al. model does not predict a mean flux counter to a pressure gradient in a horizontal system.

Several investigators, notably Kemper and Rollins (1966), Olsen (1985), and Malusis et al. (2001) found that solutes accumulate upstream when they are restricted to a greater extent than water molecules. A concentration gradient in the water is established that has the effect of increasing resistance to advection. The added resistance is caused by the tendency of water to diffuse in a direction opposite to the advective flux. The result is that a larger pressure difference must be imposed across a porous medium for a given net flux of water. This phenomenon is not predicted by any theory based on continuum mechanics.

Kemper and Rollins (1966) refer to the buildup of pressure upstream resulting from the accumulation of salts in response to an imposed pressure gradient as *osmotic pressure*. Osmotic pressure developed is less than a theoretical osmotic pressure based on the measured solute concentration because the clay soils investigated, unlike a perfect membrane, do not totally exclude solutes. The ratio of actual pressure buildup to the maximum possible osmotic pressure (corresponding to the observed concentration) is defined as *osmotic efficiency* of the soil material. Fritz (1986) presented a review of literature dealing with hyperfiltration effects and osmotic efficiency.

Mason and Malinauskas (1983) refer to the separation of constituents in response to an imposed pressure gradient on a gaseous solution as *forced diffusion*. This nomenclature follows from the definition of diffusion as a flux relative to the mean flux. However, the experiments of Kemper and Rollins (1966), Olsen (1985), and Malusis et al. (2001) show that diffusion defined in this way actually includes transport due to both pressure and concentration gradients. In a dynamic process, the relative magnitude of the two mechanisms is likely to change with time, so that evaluating mean velocity with a constitutive equation involving a single coefficient is not a valid option. Moreover, diffusion may occur in cases where no separation occurs along a flow path. An example is the case of thermal diffusion of pure water investigated by Corey and Kemper (1961).

Corey and Kemper (1961) conducted an experiment (Fig. 1) originally intended to demonstrate limitations of the total potential concept. We believe that their experiment also shows the fallacy of the Bird et al. model as it applies to thermal diffusion. Corey and Kemper established a temperature difference of 10°C across an interchangeable porous membrane separating two reservoirs filled with pure water. Initially, water levels in piezometers in both reservoirs were equal. The first membrane investigated was cellulose acetate with an estimated pore dimension of 2.7 nm. The second membrane was a Millipore (Billerica, MA) filter with an estimated pore dimension of 100 nm.

Density of water in the colder reservoir was slightly greater than density in the warmer reservoir. However,

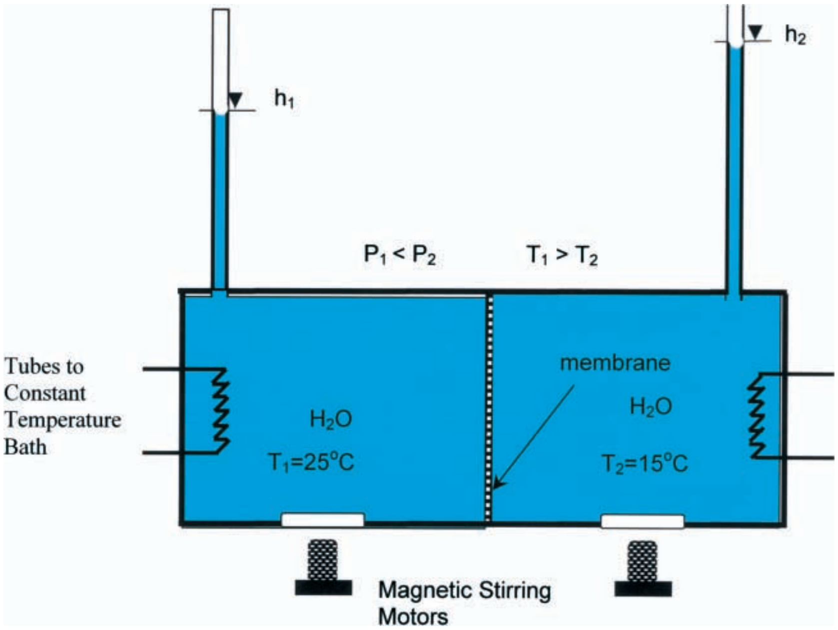

Fig. 1. Corey-Kemper experiment (1961).

the water level in the piezometer in the colder reservoir moved upward and the level in the piezometer in the warmer reservoir moved downward. A steady state was eventually established such that the levels remained constant, indicating a zero net flux across the membrane. Flux is used here to designate a velocity averaged in a cross section of medium rather than a cross section of solution. We note that since the liquid involved was pure water, diffusion as interpreted by Bird et al.(2002) was not a mechanism of transport.

The head difference at steady state with the cellulose acetate membrane was 70 cm compared with 0.9 cm with the Millipore filter. The head difference at steady state is interpreted as *thermal-induced* pressure, analogous to *concentration-induced* osmotic pressure measured by Malusis et al. (2001).

Some reviewers of the Corey and Kemper paper suggested that forces of interaction between water and the membrane material could account for the observed flux. We note that any force associated with a pure water–membrane interaction will be normal to membrane surfaces. The surface force should not affect the driving forces producing either advection or diffusion. However, resistance to flux resulting from either a pressure or temperature gradient may be affected by membrane properties, including surface forces as well as pore geometry, especially where the solution includes soluble salts.

Corey and Kemper (1961) concluded that two independent mechanisms of transport were involved in their experiment: a flux responding to a thermal gradient and a flux responding to a pressure gradient, although the solution consisted of a single molecular species. Moreover, the flux mechanisms are different functions of matrix properties. This fact makes it impossible to evaluate the average velocity with a constitutive equation involving a single coefficient where both thermal and pressure gradients exist.

We also conclude, from the Corey-Kemper observations, that barycentric velocity cannot be evaluated by the Stokes equation of fluid motion where a thermal gradient exists. Mean flux observed by Corey and Kemper (before a steady state occurred) was opposite in direction to that predicted by the Stokes equation. Consequently, a statement often found in the literature (that a temperature gradient has little effect on the mean velocity) is obviously false in the general case.

It is clear from the experimental observations described above that density and thermal gradients represent driving forces independent of a pressure gradient, as stated by Mason and Malinauskas (1983) in their paper dealing with the Dusty-Gas Model for transport of gases. Each mechanism must be evaluated independently with a transport equation involving a coefficient reflecting the resistance function associated with the particular mechanism. Net transport can be determined only by summing fluxes associated with each mechanism.

Experimental observations cited above demonstrate clearly that the Stokes equation is not adequate for evaluating mean velocity of constituents in a solution subject to density or thermal gradients. Recent authors have presented more general equations, based on the Stefan-Maxwell equations for evaluating mean velocity that involve less stringent assumptions. However, equations based on the Stefan-Maxwell model described by Truesdell and Toupin (1960), also define diffusion velocity as a velocity relative to the mean velocity. Consequently, constituent equations based on this model also are constrained by the requirement that the vector sum of diffusion fluxes is zero.

This constraint implies that diffusion does not occur in solutions consisting of a single molecular species. Consequently, the Stefan-Maxwell model, like the Bird et al. model, would define the average flux observed by Corey and Kemper (1961) as advection only, even though a major component of the flux observed was in response to a thermal gradient.

We believe that the experimental evidence cited indicates that the Bird et al. model for net velocity of a constituent in a solution is unsatisfactory. A revised model is described below.

REVISED MODEL

Our model treats diffusion as a transport mechanism that contributes to the mean flux of all constituents of a solution, as well as flux of particular constituents, relative to external coordinates. Diffusion is not regarded as a mixing process only, but rather as a flux driven by a force that is not accounted for in the Stokes equation of fluid motion. The driving force associated with concentration or thermal gradients is not consistent with theory based on continuum mechanics because it is associated with solution properties inconsistent with the continuum assumption.

The term *flux* is used here to designate a velocity averaged in a medium cross section rather than a solution cross section, because we use Darcy's equation to evaluate transport in porous media by advection.

Darcy's equation, like the Stokes equation, has no term for kinetic energy gradients associated with density or thermal gradients. A model is proposed for evaluating flux of a constituent as the vector sum of a flux responding to a pressure gradient and body force, and a flux responding to either a concentration or thermal gradient. We assume that error introduced by adding a pressure gradient and body force is negligible under most cases of interest.

We call the flux resulting from a pressure gradient and body force *advection*, and the flux responding to either a concentration or thermal gradient *diffusion*. Constitutive equations, required for the revised model, already appear in the literature.

Flux of a constituent in porous media is given by

$$\boldsymbol{q}_i = c_i\boldsymbol{q} + \boldsymbol{J}_i^N. \qquad [6]$$

The net flux of a constituent is designated as $\boldsymbol{q}_i$; the advective flux of the solution as a whole is designated as $\boldsymbol{q}$. $\boldsymbol{J}_i^N$ is the net diffusion flux of a constituent, resulting from both concentration and thermal diffusion. The diffusion flux in Eq. [6] differs from $\boldsymbol{j}_i$ in Eq. [2] because it represents a volume flux rather than a mass flux. The flux is averaged in a cross section of porous medium, including solid as well as solution, rather than a cross section of solution. Moreover, all terms in Eq. [6] are volume fluxes relative to external coordinates, not to the mean flux. Advection as defined here does not represent the mean flux of all constituents, and diffusion fluxes (as defined here) do not sum to zero in the general case.

Advection in Porous Media

Advection, unlike barycentric velocity, may be evaluated with an appropriate version of the Stokes equation where slip flux is a negligible mechanism of transport. A solution of the Stokes equation based on an assumption of zero velocity at a solid boundary significantly underestimates advective flux where channel dimensions approach the dimensions of a fluid particle. Evaluation of slip flux requires a unique coefficient because momentum is transferred directly to solid boundaries.

In most cases, slip flux in liquids probably can be neglected, although it may be a significant mechanism of transport through porous media with a very large specific surface. Slip flux for gases is a much more significant mechanism of transport than is the case for liquid solutions. Slip flux with gases is inversely proportional to pressure (Klinkenberg, 1941).

Darcy's equation can be induced from the Stokes equation for flow through porous media as has been pointed out by many authors (Bear, 1972). Experience shows that Darcy's equation is adequate for evaluating advection in soils, provided it is corrected for slip flux. However, Darcy's equation, like the Stokes equation, cannot be used to calculate barycentric flux where density and temperature gradients are significant driving forces compared with the resultant of a pressure gradient and body force.

A version of Darcy's equation consistent with the observations of Klinkenberg (1941) is given by

$$\boldsymbol{q} = (k/\mu + k_{\mathrm{s}})(\rho\boldsymbol{g} - \nabla p). \qquad [7]$$

The advective flux vector appearing in Eq. [7] differs from $\boldsymbol{v}$ in that $\boldsymbol{q}$ is averaged in a cross section of porous matrix rather than a cross section of solution. The coefficient k is intrinsic permeability with dimensions of length squared, and k_{s} is a coefficient, independent of viscosity, accounting for slip flux. Forces representing gravity and pressure gradient appear as separate terms in Eq. [7], and the coefficient for viscous flow is intrinsic permeability divided by viscosity, so that Eq. [7] is applicable for gaseous as well as liquid solutions.

The advective flux vector evaluated by Eq. [7] is a volume flux. We note that Darcy's equation is strictly valid only for volume flux. Error from evaluating mass or molar flux with Darcy's equation is negligible in the case of liquid solutions. However, error from employing Darcy's equation to evaluate mass or molar flux for gases, subject to varying absolute pressures, can be significant. Viscosity is not a function of gas density, but density of gas is a function of absolute pressure, so that resistance to gas flow is proportional to volume flux only. Mass or molar flux is not a linear function of a pressure gradient (Klinkenberg, 1941).

Equation [7] is inadequate for cases where resisting or driving forces on different molecular or ionic species are unequal, such as in the cases studied by Kemper and Rollins (1966), Olsen (1985), and Malusis et al. (2001). In such cases, a gradient of solutes in the water solution undoubtedly leads to a gradient of effective permeability to the solvent. Experimental or theoretical descriptions of the relationship between solute concentration and effective solvent permeability are not currently available. For an analysis of electrokinetic effects on hydraulic and osmotic flow of ions through clays, the reader is referred to a paper by Kemper et al. (1972), and to the other authors on this subject cited in their paper.

Diffusion in Porous Media

We interpret diffusion as the flux of a constituent (relative to fixed coordinates) in response to concentration or thermal gradients. This interpretation is consistent with the interpretation of Fick and other early investigators such as Thomas Graham (1833) and those who verified his observations. It is not consistent with the Bird et al. model or other closely related models described in modern textbooks.

In deriving an equation for diffusion, Bird et al. (2002) subtracted what they interpreted as the mean velocity from the velocity of a constituent relative to fixed coordinates. We consider that the Bird et al. model is invalid because transport they interpreted as mean flux is actually only a component of mean flux responding to a piezometric gradient, as shown by the experimental observations cited above. Consequently, we evaluate mean flux with the equation set presented above for the revised model. Diffusion fluxes do not sum to zero in the general case, as demonstrated by experimental observations.

In deriving a constitutive equation for a velocity relative to fixed coordinates, we assume that the number of constituent molecules crossing a reference surface within a given time interval is proportional to the product of concentration and the mean velocity of constituent molecules. We assume that a pressure gradient has negligible effect on diffusion in a liquid solution, because it has no effect on concentration for incompressible fluids.

We conceptualize fluid particles to be moving relative to fixed coordinates with a velocity responding to a piezometric gradient. The term *fluid particle* does not refer to a physical entity in the usual sense. It is an abstraction, and the velocity we assign to fluid particles is also an abstraction. Particle velocity, in the case of fluids that are not continua, is not synonymous with mean velocity as defined by Bird et al. (2002).

We designate molecular velocity in a frame of reference attached to a fluid particle as $\boldsymbol{s}$. Molecular velocity for an ideal gas, in a frame of reference attached to a fluid particle, is directly proportional to the square root of Kelvin temperature and inversely proportional to the square root of molecular mass.

For an ideal gas,

$$\boldsymbol{s}_i \propto T^{1/2} M_i^{-1/2}, \tag{8}$$

where T is Kelvin temperature; M_i is molecular mass, and $\boldsymbol{s}_i$ is an average molecular velocity of a constituent in a frame of reference attached to a fluid particle. For the general case of liquid solutions,

$$\boldsymbol{s}_i \propto M_i^{-1/2} f(T). \tag{9}$$

Kinetic energy of ideal gas molecules proportional to Kelvin temperature, according to kinetic theory, is due to the velocity of translation in a frame of reference attached to fluid particles. Intermolecular forces restrict the mean free path of liquid molecules so that kinetic energy may be partly due to rotation or vibration rather than translation only. According to kinetic theory, the driving force for thermal diffusion is a gradient of kinetic energy. We assign the dimensions of energy per unit mass to temperature so that the gradient of temperature multiplied by density represents force per unit volume. However, only a portion of the temperature gradient is effective in transporting mass. A large portion of the temperature gradient is effective in transporting heat only.

We assume that the proportion of a temperature gradient effective in transporting mass depends on the extent to which the velocity of translation is restricted by intermolecular forces. For example, a temperature gradient in a solid results in no mass transport by diffusion. The temperature gradient obviously is dissipated entirely by flow of heat rather than mass in this case.

Diffusion is related to the gradient of a function of temperature, not to temperature per se, because a temperature gradient can affect diffusion only to the extent that velocity of translation of fluid molecules is affected. Unfortunately, experimental data (identifying an appropriate function of temperature for liquid solutions) is not available in the literature. For gaseous solutions, one may assume a suitable function is $T^{1/2}$ based on kinetic theory as described above.

We expect that an appropriate function for all fluids also will be proportional to $T^{1/2}$, and the effect of intermolecular forces on reducing the velocity of translation of liquid molecules is likely to be limited to a reduction of the diffusion coefficient of liquids compared with gases. However, the latter prediction is based on speculation only. Research to establish a quantitative relationship between diffusion and a thermal gradient is needed, especially for water.

On the basis of the reasoning described above, a tentative constitutive equation is proposed for thermal diffusion:

$$\boldsymbol{J}_i^T = -D_i T^{-1/2} \nabla T^{1/2}, \tag{10}$$

where D is a diffusion coefficient depending on constituent, solution, and porous medium properties, and is inversely proportional to the square root of molecular mass, and $\boldsymbol{J}^T$ is diffusion flux responding to a thermal gradient. Fick's law in response to a concentration gradient, generalized for volume flux in porous media, is given by

$$\boldsymbol{J}_i^c = -D_i c^{-1} \nabla c_i. \tag{11}$$

Net diffusion flux is given by

$$\boldsymbol{J}_i^N = \boldsymbol{J}_i^c + \boldsymbol{J}_i^T. \tag{12}$$

For diffusion of a constituent in a gas, c is a function of pressure and temperature as well as mole fraction. A more detailed analysis of diffusion of gaseous constituents is presented in Appendix B.

Thought Experiment

A thought experiment is presented below to show the contrast in conclusions resulting from the Bird et al.

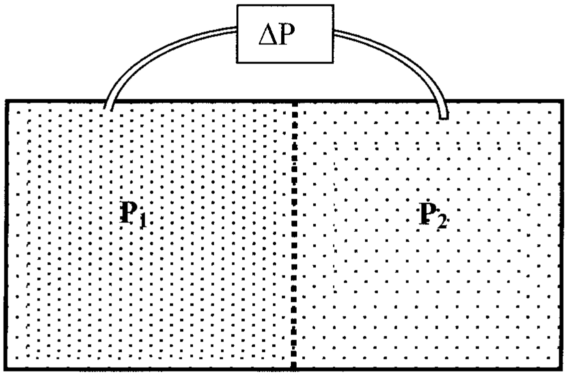

Fig. 2. Thought experiment.

model and our revised model. Figure 2 represents a chamber separated into two parts by a porous membrane containing a binary gas with constituents having different molecular masses.

Initially, the mole fractions of the two constituents are equal on both sides of the membrane. Pressure on both sides is also equal. The absolute pressure on the right is then reduced so that $p_1 > p_2$. Both models predict that a net flux will occur from left to right across the membrane until equal pressures and concentrations are established on both sides.

The Bird et al. model predicts that since the mole and mass fractions are initially equal on both sides of the membrane, the initial flux will be exclusively advection as evaluated by Stokes equation. The revised model predicts that because the concentrations of both constituents on the right are less than that on the left, diffusion of both constituents, as well as advection, will occur from left to right. Diffusion fluxes for the two constituents predicted with the revised model will not sum to zero. The total flux will be the sum of fluxes by advection and diffusion, a greater flux than that evaluated by the Stokes equation. The ratio of fluxes due to advection and diffusion will depend on dimensions of channels in the membrane.

Support for the revised model is based primarily on experimental evidence. However, for those who prefer an explanation in mathematical terms, an analysis is presented in Appendix A.

Pressure Related to Normal Surface Stress

The reason that Bird et al. (2002) and others assume mean flux is evaluated by the Stokes equation is, evidently, because they believe gradients of density, or velocity of molecular translation associated with temperature, are reflected in the pressure gradient. Consequently, it is important to understand why gradients of density or molecular velocity are not entirely reflected in a pressure gradient. The reason is that a directional variation in normal surface stress does not contribute to a pressure gradient. Only a spatial variation in normal surface stress contributes to a pressure gradient.

Streeter (1948) shows that pressure is given by

$$p = (\sigma_x + \sigma_y + \sigma_z)/3. \qquad [13]$$

In Eq. [13], σ_x, σ_y, and σ_z are magnitudes of the normal surface stress vector $\boldsymbol{\sigma}$ in three coordinate directions. Normal surface stress represents rate of change of momentum averaged in a reference area rather than the entire surface of a reference volume. Both pressure and normal surface stress are intensive variables because they are defined at a point, the centroid of differential elements across which momentum is averaged. An area is regarded as a vector having the direction of the outer normal, as explained in all textbooks dealing with vectors. Consequently, normal surface stress, unlike pressure, is a vector quantity, and its magnitude varies with direction relative to the resultant velocity.

Normal stress is associated with the number and velocity of molecules crossing a surface area. If there is no resultant velocity, there is no directional variation in $\boldsymbol{\sigma}$. The magnitude of $\boldsymbol{\sigma}$ is equal in all directions and equal to p in static systems because the resultant molecular velocity is zero in this case. Pressure in a static system varies in space only in the direction of a body force, and the body force balances the pressure gradient.

Pressure is measured with a piezometer provided the open tip is oriented in the solution so that it produces no stagnation of flow; that is, the plane of the opening is parallel to the resultant molecular velocity. When properly oriented, a piezometer will measure the average magnitude of normal surface stress components. By contrast, a Pitot tube is oriented to produce stagnation at its tip so that it responds to impact of fluid molecules normal to the plane of the tube opening.

Conceptually, a Pitot tube could be used to measure a directional variation in the magnitude of $\boldsymbol{\sigma}$. However, directional variation in $\boldsymbol{\sigma}$ is associated with advection as well as diffusion. Only the rate of change of momentum in a frame of reference attached to a reference volume drives diffusion. Moreover, the directional variation in normal surface stress is nearly always too small compared with the pressure to be detected by a Pitot tube.

The rate of angular deformation, for a given local velocity, increases rapidly with decreasing channel dimensions. Specifically, resistance increases with the inverse square of channel dimensions, as predicted by Poiseuille's equation for viscous flow in tubes. As channel dimensions approach the mean free path of fluid molecules, resistance to viscous flow would theoretically approach infinity if slip at solid boundaries did not occur.

Advective flux through channels smaller than the mean free path, in response to a pressure gradient, is due to *slip flux* and results in transfer of momentum from moving molecules directly to solid boundaries. Knudsen (1909) was the first to report slip flux for flow of liquids under large pressure gradients in very small tubes. He interpreted slip flux as being associated with a nonzero velocity where fluid contacts a solid surface. A coefficient relating resistance to slip flux does not involve fluid viscosity directly. A velocity component resulting from directional variation in surface stress, associated with diffusion, involves a different mechanism of momentum transfer to solid boundaries that apparently causes no angular deformation of volume elements.

CONCLUSIONS

(i) Advection, defined as velocity responding to the resultant of body force and a pressure gradient, is a component of the total velocity, not the mean velocity of all constituents in a solution. (ii) Advection in porous media includes slip flux as well as viscous flux. (iii) Diffusion, defined as a velocity responding to concentration and thermal gradients, is a velocity component relative to a fixed frame of reference external to the solution, not to the mean or barycentric velocity. (iv) Forces producing diffusion are independent of forces producing advection. (v) Resistance to advection and diffusion are different functions of matrix properties.

APPENDIX A—ANALYSIS

Resistance associated with slip flux, $\boldsymbol{r}_s$, is a function of pressure and advective flux, as well as fluid and media properties. Slip at the boundary causes an overall reduction in resistance to advection because of a reduction in fluid rotation, and a reduction in the associated viscous resistance, in channels of a given dimension. The velocity profile normal to channel boundaries is to some extent flattened by slip at the boundaries. Resistance associated with diffusion, $\boldsymbol{r}_i$, is a function of temperature and diffusion flux as well as constituent, fluid, and medium properties, but diffusion produces no fluid rotation or viscous resistance. Evidence supporting Darcy's equation shows that tangential acceleration can be neglected for flow in porous media where diffusion is a significant mechanism of transport. Resistance forces balance driving forces virtually instantaneously in the latter case.

Molecules in fluid particles possess kinetic energy associated with their motion. Where concentration or temperature gradients exist, this energy is capable of transporting mass as well as heat. Molecular motion is not entirely random relative to coordinates attached to a fluid particle. In this case, molecules have a resultant velocity in the direction of decreasing concentration or temperature. The force producing the resultant velocity is a gradient of kinetic energy in a frame of reference attached to fluid particles. A concentration gradient contributes to the force because concentration gradients usually are associated with a gradient of density.

Stokes equation may be modified formally to include diffusion for solutions subjected to significant concentration and thermal gradients as

$$\rho\boldsymbol{g} - \nabla p + \mu\nabla^2\boldsymbol{v} + \boldsymbol{r}_s - \sum_1^n \nabla(\rho_i \boldsymbol{s}_i^2/2) + \sum_1^n \boldsymbol{r}_i = 0 \qquad [14]$$

The fifth term on the left of Eq. [14] evaluates the driving force per unit volume of solution for diffusion. The diffusion flux considered here is a component of the net or mean volume flux of all constituents in the solution relative to external coordinates. It is not a flux relative to the barycentric flux.

We present Eq. [14] to explain our analysis of diffusion and advection, but not as a method of evaluating mean velocity. Advection, associated with the first four terms on the left of Eq. [14], is evaluated with Eq. [7]. Diffusion, associated with last two terms on the left of Eq. [14] is evaluated with Eq. [10] and [11].

The equations of Stefan-Maxwell include terms for divergence, tangential acceleration, and momentum resulting from chemical reactions not appearing in Eq. [14]. We have omitted forces of divergence and tangential acceleration because experience shows them to be unimportant for cases where diffusion is a significant mechanism of transport. However, the equations of Stefan-Maxwell omit momentum flux associated with concentration and thermal gradients, because the continuum assumption is accepted in their derivation.

We believe this omission invalidates the Stefan-Maxwell model as well as the Bird et al. model for conceptualizing diffusion and advection. We also believe this omission has led many authors to conclude, incorrectly, that species velocities in response to concentration or thermal gradients must sum to zero, and that they have no effect on mean velocity. Our model predicts that the only case for which a concentration gradient would not contribute to average velocity is where all molecular species, undergoing isobaric and isothermal interdiffusion, have identical molecular masses. In the latter case, the last two terms on the left of Eq. [14] independently sum to zero. We can conceive of no case such that these terms would vanish where a temperature gradient is involved.

APPENDIX B—DIFFUSION OF CONSTITUENTS OF IDEAL GASES

Concentration is a function of Kelvin temperature and absolute pressure for gases. The ideal gas law for most gases of interest can closely approximate the relationship. In this case, the constitutive equation for diffusion in response to both concentration and temperature gradients is conveniently written as a single flux equation. Diffusion is assumed to be directly proportional to the gradient of the product of concentration and velocity of molecular translation in a frame of reference attached to a fluid particle.

Combining Eq. [8] and the ideal gas law indicates that the product of concentration and velocity of translation is given by

$$\boldsymbol{s}_1 c_i = p_i T^{-1/2}/RM^{1/2}, \qquad [15]$$

where R is the universal gas constant, and p_i is the partial pressure of the constituent. A tentative constitutive equation for diffusion of gaseous constituents in response to either temperature or concentration gradients is given as

$$J_i^N = -D_i p^{-1} T^{1/2} \nabla (p_i T^{-1/2}). \qquad [16]$$

Eq. [16], like Eq. [10], is based exclusively on theoretical considerations and needs experimental verification. The theory indicates that, because concentration is inversely related to Kelvin temperature and molecular velocity is directly related to only the square root of temperature, the net effect of a temperature gradient for gases is a diffusion flux in the opposite direction to that for thermal diffusion in liquid solutions.

Bird et al. (1960) state that "temperature gradients, and external forces also contribute to the diffusion flux, although their effects are usually minor." In fact, the indirect effects of a pressure gradient on diffusion of gaseous constituents can be large. A temperature gradient can have a significant indirect effect on diffusion of gaseous constituents, and a direct effect on diffusion of constituents in liquids that is not necessarily small.

APPENDIX C

List of Symbols

Mass (M), Length (L), and Time (T)

Velocity Vectors†

$\boldsymbol{v}$ advective solution velocity (volume/solution area/time) relative to external coordinates ($\mathrm{L\ T^{-1}}$)

$\boldsymbol{q}$ advective solution flux, (volume/medium area/time) relative to external coordinates ($\mathrm{L\ T^{-1}}$)

$\boldsymbol{J}^N$ net diffusion flux (volume/medium area/time) responding to concentration and thermal gradients ($\mathrm{L\ T^{-1}}$)

$\boldsymbol{J}^c$ diffusion flux responding to concentration gradients ($\mathrm{L\ T^{-1}}$)

$\boldsymbol{J}^T$ diffusion flux responding to thermal gradients ($\mathrm{L\ T^{-1}}$)

$\boldsymbol{s}$ molecular velocity (in all directions) relative to coordinates attached to fluid particles ($\mathrm{L\ T^{-1}}$)

$\boldsymbol{j}$ diffusion mass flux, (as defined by Eq. [1]) ($\mathrm{M\ L^{-2}\ T^{-1}}$)

$\boldsymbol{j}^\dagger$ diffusion molar flux (as evaluated by Eq. [4]) ($\mathrm{L^{-2}\ T^{-1}}$)

Resistance Vectors

$\boldsymbol{r}_s$ resistance to advection associated with slip flux ($\mathrm{M\ L^{-2}\ T^{-2}}$)

$\boldsymbol{r}_i$ resistance to diffusion of a constituent ($\mathrm{M\ L^{-2}\ T^{-2}}$)

State Variables

p pressure ($\mathrm{M\ L^{-1}\ T^{-2}}$)

T temperature ($\mathrm{L^2\ T^{-2}}$)

t time (T)

$\boldsymbol{\sigma}$ normal surface stress ($\mathrm{M\ L^{-1}\ T^{-2}}$)

c molar concentration ($\mathrm{L^{-3}}$)

ρ solution or constituent density ($\mathrm{M\ L^{-3}}$)

$\boldsymbol{g}$ body force vector ($\mathrm{L\ T^{-2}}$)

Coefficients

$\mathfrak{D}$ diffusion coefficient in Eq. [3] and [4] ($\mathrm{L^2\ T^{-1}}$)

D_i diffusion coefficient in the revised model, a function of temperature, constituent, medium, and solution properties ($\mathrm{L^2\ T^{-1}}$)

k intrinsic permeability to solution ($\mathrm{L^2}$)

k_s coefficient for slip flux ($\mathrm{L^3\ M^{-1}\ T}$)

μ dynamic viscosity ($\mathrm{M\ L^{-1}\ T^{-1}}$)

Subscripts

$_i$ indicates a particular constituent (none)

$_{x,y,z}$ indicate coordinate directions (none)

$_s$ indicates slip flux (none)

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† All velocity and flux variables are resultant velocities in the tangential direction, except $\boldsymbol{s}$ which implies no particular direction.

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