Applicability of Fick's Law to Gas Diffusion[1]

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ABSTRACT

The comparison of Fick's Law for the diffusion of gas i in a vapor to the equations based on the kinetic theory of gases shows that only for certain special conditions is the Fickian diffusion coefficient, D_{F_i}, independent of the mole fraction of i and the diffusional fluxes of the other gases. These conditions include the diffusion of a trace concentration of gas through a gas mixture of any composition, equimolar, counter-current diffusion in a binary gas mixture, and diffusion in a ternary mixture where one gas is stagnant. In an O_2, CO_2, N_2 atmosphere, variations in diffusion coefficient of at least 10% from the tracer values are possible with variations in the mole fractions of the gas or the relative magnitude of their fluxes. The temperature and pressure dependency of the diffusion coefficient must also be recognized.

Additional Index Words: diffusion coefficient, binary diffusion coefficients, Stefan–Maxwell equations.

THE EXCHANGE OF GASES between the soil and the atmosphere is of primary concern to soil scientists. Gas movement in the soil can be caused by both convection and diffusion. Convection results when a difference in total gas pressure exists between two locations. Diffusion will occur even if the total pressure is uniform as long as there is a spatial difference in the chemical potential, normally represented by differences in concentration or partial pressure, of the components of a gas mixture (Kittel, 1969). While both processes are important in soils, diffusion is considered to dominate during normal gaseous exchange (Evans, 1965).

The fundamental equation used to describe one-dimensional, steady-state diffusion in soil is Fick's First Law:

$$q_i = -\alpha D_{F_i} dC_i/dz , \qquad [1]$$

where q_i is the mass transfer rate of component i per unit area ($ML^{-2}T^{-1}$), D_{F_i} is the Fickian diffusion coefficient for component i (L^2T^{-1}), C_i is the concentration of i (ML^{-3}), z is distance, and α is a correction term that modifies D_{F_i} to account for the air-filled porosity and the tortuosity of the diffusion path in soils (Troeh et al., 1982). Although the magnitude of α is often crucial in the study of diffusional processes in soils, in the remainder of this paper the magnitude of α is inconsequential as long as its magnitude is independent of gas type (Penman, 1940b). We will therefore set α equal to 1.0 and drop it from the remaining equations.

Alternatively, Eq. [1] can be written in terms of mole fractions by invoking the equation of state for ideal gases and Dalton's Law to give

$$N_i = -D_{F_i}(P/RT)dY_i/dz , \qquad [2]$$

where now N_i is the molar flux, P is the total gas pressure, R the universal gas constant, T absolute temperature, and Y_i the mole fraction of component i. While useful in soil science, it must be remembered that Fick's Law when applied to gases is strictly an empirical relation, borrowed from studies with solutes and shown to agree well with observed diffusional processes in air (Kirkham and Powers, 1972, p. 429; Penman, 1940a and 1940b). The form of Eq. [2], the flux of a gas being equal to its gradient multiplied by a simple coefficient, is very misleading and requires closer examination.

The equations for gaseous diffusion were developed by Stefan (in Wilke, 1950) and Maxwell (1952) among others. The equations are based on the statistical mechanics description of ideal gases developed by Gibbs and Boltzmann (Kittel, 1969). These equations have been extensively developed in the literature and found to agree very closely with experiments on gas diffusion, especially at near normal temperatures and pressures (Hirschfelder et al., 1964; Fairbanks and Wilke, 1950). Since the interest in gas diffusion in soils has increased in recent years (Smith, 1977; Bakker and Hidding, 1970; DeJong et al.,

1979, and others) and Fick's Law is used to describe the process in most soils literature (see Wood and Greenwood, 1971, for an exception), it would seem advisable to compare Fick's Law (Eq. [2]) to the Stefan–Maxwell diffusion equations in order to gauge its validity. This paper will examine several simple cases of diffusion of interest in soil science. It is not our intention to develop the Stefan–Maxwell equations in depth, nor to fully present the theory underlying them. For this, the reader is directed to the comprehensive works by Chapman and Cowling (1939) or Hirschfelder et al. (1964), or to the excellent review by Marrero and Mason (1972). We shall, for the remainder of the paper, consider only diffusion in the gas phase, ignoring gas–liquid interactions, convection, turbulence, or other mass flow phenomena, and for simplicity will consider only steady-state diffusion, although the results are directly applicable to the non-steady-state case.

STEFAN–MAXWELL EQUATIONS FOR GAS DIFFUSION

Chapman and Cowling (1939, p. 244) have shown that for diffusion, the average velocity of one gas in relation to a second gas is represented by

$$\bar{v}_i - \bar{v}_j = -\frac{n_T^2}{n_i n_j} D_{ij} \left[\frac{\partial(n_i/n_T)}{\partial r} + \frac{n_i n_j (m_j - m_i)}{\rho_T n_T} \frac{\partial \ln P}{\partial r} \right.$$

$$\left. - \frac{\rho_i \rho_j}{P(\rho_i + \rho_j)}(F_i - F_j) \right.$$

$$\left. + \frac{D_T}{D_{ij} T} \partial T/\partial r \right], \qquad [3]$$

where the terms are defined at the end of this paper. For our purposes, it is only important to note that the difference in average velocities of two gases $(\bar{v}_i - \bar{v}_j)$ depends on four separate terms on the right side of Eq. [3], which may be thought of as the chemical potential for the gas pair (Kittel, 1969, p. 215). The first term represents ordinary or concentration diffusion, which we are concerned with in this paper. The second term represents diffusion caused by differences in total pressure, but should not be confused with mass flow. As an example of pressure diffusion, lighter elements such as helium will concentrate in the upper portions of the atmosphere due to diffusion driven by pressure differences in the atmosphere. The gases respond to the pressure gradient created by gravity and not to gravity directly. The third term represents a diffusional flux created by an external force, such as a flow of charged particles in an electric field giving rise to an electric current. The final term represents thermal diffusion. In thermal diffusion, a temperature difference will cause diffusion within a gas mixture, with the lighter components concentrating near the warmer zone. If the temperature gradient is maintained, the gas components will continue to separate until ordinary diffusion exactly balances thermal diffusion. Of the four terms, only concentration or ordinary diffusion is important under normal circumstances in soil and plant processes, although thermal diffusion is used in commercial refining techniques for separating isotopes of some gases (Jones and Furry, 1946; Vasaru et al., 1969).

For ordinary diffusion in one dimension of one gas, i, through another gas, j, where total pressure and temperature are constant, Eq. [3] reduces to

$$\bar{v}_i - \bar{v}_j = -\frac{n_T^2}{n_i n_j} D_{ij} \frac{d(n_i/n_T)}{dz}. \qquad [4]$$

Dividing by

$$\frac{n_T}{n_i n_j} D_{ij},$$

Eq. [4] can be rearranged such that

$$\frac{\bar{v}_i n_i n_j - \bar{v}_j n_j n_i}{n_T D_{ij}} = -n_T \frac{d(n_i/n_T)}{dz}. \qquad [5]$$

Dividing both sides of Eq. [5] by Avagadro's number, M_o, we convert the number densities to molar densities. Remembering that $N_i = v_i n_i/M_o$, Eq. [5] becomes

$$\frac{N_i n_j - N_j n_i}{n_T D_{ij}} = -\frac{n_T}{M_o} \frac{d(n_i/n_T)}{dz}. \qquad [6]$$

But since $Y_i = n_i/n_T$ and for unit volume $n_T/M_o = P/RT$ Eq. [6] reduces to

$$\frac{N_i Y_j - N_j Y_i}{D_{ij}} = -\frac{P}{RT} \frac{dY_i}{dz}, \qquad [7]$$

and D_{ij} is the mutual diffusion coefficient for gases i and j.

In a multicomponent gas mixture, the diffusion of component i can be represented by a linear summation of Eq. [7] for each gas pair (Curtiss and Hirschfelder, 1949). The equations for diffusion of each component in an n-component mixture commonly referred to as the Stefan–Maxwell equations are

$$-\frac{P}{RT} dY_i/dz = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{N_i Y_j - N_j Y_i}{D_{ij}}. \qquad [8]$$

We should note that D_{ij} in Eq. [8] is not identical to the binary D_{ij} in Eq. [7], since its magnitude is affected by the entire gas mixture and not just i and j. However, this difference is slight (within the experimental error of measurement) and can be ignored (Marrero and Mason, 1972).

In general, Eq. [8] represents n-1 independent equations for n unknowns since

$$\sum_{i=1}^{n} Y_i = 1.0$$

and as such the solution is indeterminate. However, under certain simplifying assumptions solutions can be found for the series of equations. We'll examine several of these situations applicable to soil and plant science.

BINARY GAS SYSTEM

For the simplest case of diffusion in a two-component system (i and j), Eq. [8] yields only one unique equation, identical to Eq. [7], since $Y_i + Y_j = 1.0$. Equation [7] can be rearranged into a form similar to Fick's Law (Eq. [2]). By letting r_{ji} equal the negative value of the ratio of the fluxes, $r_{ji} = -N_j/N_i$, and substituting $1-Y_i$ for Y_j, we can rearrange Eq. [7] to obtain

$$N_i = \frac{-D_{ij}}{1 - (1 - r_{ji})Y_i} \frac{P}{RT} dY_i/dz \ . \qquad [9]$$

Comparing Eq. [9] and Eq. [2] we find by analogy that

$$D_{F_i} = \frac{D_{ij}}{1 - (1 - r_{ji})Y_i} \ . \qquad [10]$$

The Fickian diffusion coefficient depends not only on D_{ij} but also on the flux ratio and mole ratio of component i. Two special circumstances immediately follow from Eq. [10].

Tracer Diffusion——In cases where Y_i is present only in trace amounts (i.e., $Y_i \simeq 0.0$), Eq. [10] for the Fickian diffusion coefficient reduces to

$$D_{F_i} = D_{ij} \ , \qquad [11]$$

independent of flux ratios and concentration.

Closed System—A second possibility for binary gas diffusion is diffusion in a closed system where, since the total pressure remains constant, $N_i = -N_j$, $r_{ji} = 1.0$ and, from Eq. [10], D_{F_i} again just equals D_{ij}.

Open System—A more general situation is the steady-state diffusion of gases through an inert layer where the concentrations of the gases are held constant at one end because of an infinite source/sink for the gases (the atmosphere) and the concentrations are fixed at the other end by consumption or production processes. An example would be oxygen diffusing into a soil ped and oxidizing ferrous to ferric iron where oxygen and nitrogen comprise the ped atmosphere. For an open system Eq. [9] and Eq. [10] cannot be solved without a priori knowledge of r_{ji}. Figure 1 illustrates the variation of D_{F_i} with changes in r_{ji} and Y_i as calculated by Eq. [10]. The reduced Fickian diffusion coefficient, D_{F_i}/D_{ij}, is plotted for several values of r_{ji} over the range $0.0 \le Y_i \le 1.0$. As discussed for equimolar, counter-current diffusion in a closed system and for tracer diffusion, D_{F_i}/D_{ij} is constant for all values of Y_i when $r_{ji} = 1.0$ and for all values of r_{ji} when $Y_i \simeq 0.0$. The reduced Fickian diffusion coefficient diverges rapidly, however, as Y_i increases, decreasing as r_{ji} becomes less (reduced resistance to diffusion) and increasing as r_{ji} increases. In the extreme it can be seen from Eq. [10] that D_{F_i}/D_{ij} can become negative when the two gases are diffusing in the same direction ($r_{ji} < 0.0$), that is, gas i would diffuse against its gradient. This behavior has been measured by Duncan and Toor (1962) in a three-component gas mixture.

THREE-COMPONENT GAS SYSTEMS

The soil atmosphere can normally be characterized as a three-component (ternary) system. In a ternary system composed of gases i, j, and k, where $Y_i + Y_j + Y_k = 1$, Eq. [8] yields two unique equations:

$$-\frac{P}{RT} dY_i/dz = \frac{N_i Y_j - N_j Y_i}{D_{ij}} + \frac{N_i Y_k - N_k Y_i}{D_{ik}} \ , \qquad [12]$$

$$-\frac{P}{RT} dY_j/dz = \frac{N_j Y_i - N_i Y_j}{D_{ij}} + \frac{N_j Y_k - N_k Y_j}{D_{jk}} \ . \qquad [13]$$

Again, the general solution of these equations is impossible without further simplifying assumptions.

Tracer Diffusion—If we let component i represent a gas at trace concentration ($Y_i \simeq 0.0$), so that $Y_j + Y_k \simeq 1$, then Eq. [12] which describes the diffusion of i, becomes

$$-\frac{P}{RT} dY_i/dz = N_i \left(\frac{Y_j}{D_{ij}} + \frac{Y_k}{D_{ik}} \right) , \qquad [14]$$

or, upon solving for N_i,

$$N_i = \frac{-D_{ij}D_{ik}}{Y_j D_{ik} + Y_k D_{ij}} \frac{P}{RT} dY_i/dz \ . \qquad [15]$$

This equation is identical in form to the equation for Fick's Law with the Fickian diffusion coefficient dependent only on D_{ij}, D_{ik}, and the mole fractions Y_j and Y_k:

$$D_{F_i} = \frac{D_{ij}D_{ik}}{Y_j D_{ik} + Y_k D_{ij}} \ . \qquad [16]$$

In general, for tracer diffusion in an n-component gas mixture, the tracer will diffuse according to Fick's Law, where the diffusion coefficient is equal to

$$D_{F_i} = \prod_{\substack{j=1 \\ j \ne i}}^{n} D_{ij} \bigg/ \sum_{\substack{j=1 \\ j \ne i}}^{n} \left[Y_j \left[\prod_{\substack{k=1 \\ k \ne i \, \text{or} \, j}}^{n} D_{ik} \right] \right] , \qquad [17]$$

and is independent of the diffusional fluxes of the other components.

One Gas Stagnant—Equations [12] and [13] can also be simplified if we assume one of the gases is stagnant. This is analogous to quasisteady-state respiration in a soil where oxygen and carbon dioxide are being exchanged with the atmosphere and nitrogen, the third gas com-
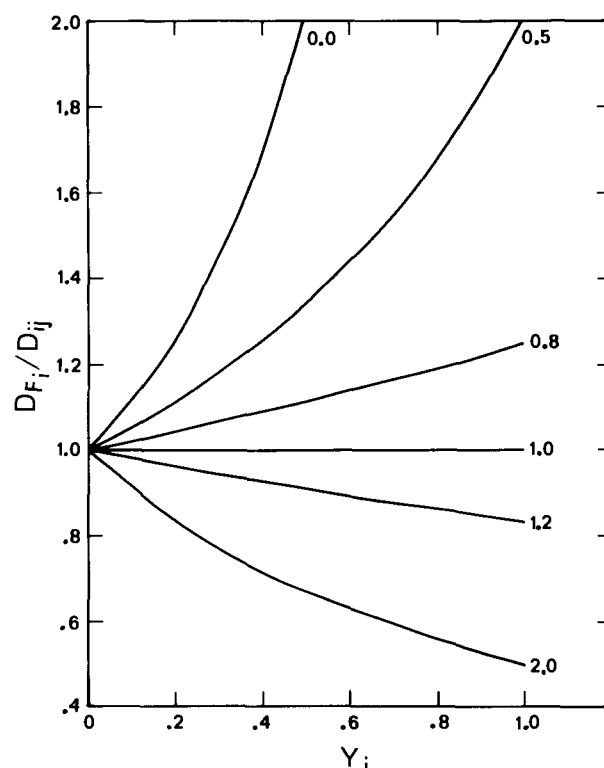

Fig. 1—Values of the reduced Fickian diffusion coefficient, D_{F_i}/D_{ij}, in a binary gas mixture plotted against the gas mole fraction of component i. Curve labels are the values of the flux ratio, r_{ji}, for which the curve was calculated.

ponent, (k), is stagnant. In the case with $N_k = 0.0$, Eq. [12] and Eq. [13] become

$$-P/RT\, dY_i/dz = N_i\left(\frac{Y_j}{D_{ij}} + \frac{Y_k}{D_{ik}}\right) - N_j\frac{Y_i}{D_{ij}}\ ,\quad [18]$$

$$-P/RT\, dY_j/dz = N_j\left(\frac{Y_i}{D_{ij}} + \frac{Y_k}{D_{jk}}\right) - N_i\frac{Y_j}{D_{ij}}\ .\quad [19]$$

These equations can be solved for the molar fluxes N_i and N_j if Y_i, Y_j and Y_k are known. In the case of counter-current, equimolar diffusion, where $N_i = -N_j$ $(r_{ji} = 1.0)$, Toor (1957) has solved these equations exactly and found that the solution must simultaneously satisfy Eq. [20] and Eq. [21].

$$N_i = -N_j = \frac{D_{ik}D_{jk}}{D_{jk} - D_{ik}}\frac{P}{RTz}\ln\frac{Y_{k_2}}{Y_{k_1}}\ ,\quad [20]$$

$$\left(1 - \frac{D_{ij}}{D_{jk}}\right)(Y_{i_1} - Y_{i_2}) + \left(1 - \frac{D_{ij}}{D_{ik}}\right)(Y_{j_1} - Y_{j_2})$$

$$= \ln Y_{k_2}/Y_{k_1}\ .\quad [21]$$

The second subscript on Y refers to the points 1 and 2 separated by distance z. These equations can be used to describe diffusion in soils where the source and sink terms for O_2 (i) and CO_2 (j) are determined by plant root or soil organism respiration and the respiration quotient, CO_2 produced/O_2 consumed, is near 1.0 (e.g., $r_{ji} = 1.0$). However, it must be remembered that this is only a good approximation for respiration in soils during quasisteady-state conditions because if Y_i or Y_j is changing rapidly, $N_k = 0.0$ and the simplification is not justified.

In general, we can solve Eq. [18] and Eq. [19] only if the ratio r_{ji} is known. Substituting $-r_{ji}N_i$ for N_j in Eq. [18] and solving for N_i and substituting $-N_j/r_{ji}$ for N_i and solving for N_j in Eq. [19] yields

$$N_i = \frac{-D_{ij}D_{ik}}{D_{ik}Y_j + D_{ij}Y_k + r_{ji}D_{ik}Y_i}\frac{P}{RT}dY_i/dz\ ,\quad [22]$$

$$N_j = \frac{-D_{ij}D_{jk}}{D_{jk}Y_i + D_{ij}Y_k + D_{jk}Y_j/r_{ji}}\frac{P}{RT}dY_j/dz\ ,\quad [23]$$

which are in the form of Fick's Law with diffusion coefficients

$$D_{F_i} = \frac{D_{ij}D_{ik}}{D_{ik}Y_j + D_{ij}Y_k + r_{ji}D_{ik}Y_i}\ ,\quad [24]$$

$$D_{F_j} = \frac{D_{ij}D_{jk}}{D_{jk}Y_i + D_{ij}Y_k + D_{jk}Y_j/r_{ji}}\ .\quad [25]$$

These equations demonstrate that the apparent diffusion coefficient in Fick's Law depends not only on the binary diffusion coefficients but also on the gas composition and the flux ratio, r_{ji}. As an example, D_F can be calculated for O_2 from Eq. [24] and for CO_2 from Eq. [25] in a ternary atmosphere where $i = O_2$, $j = CO_2$, $k = N_2$, and $N_{N_2} = 0.0$. For this case Eq. [24] and Eq. [25] become.

$$D_{F_{O_2}} = \frac{D_{O_2,CO_2}D_{O_2,N_2}}{D_{O_2,N_2}Y_{CO_2} + D_{O_2,CO_2}Y_{N_2} + r_{CO_2,O_2}D_{O_2,N_2}Y_{O_2}}\ ,$$

$$D_{F_{CO_2}} = (D_{O_2,CO_2}D_{CO_2,N_2})/\big[D_{CO_2,N_2}Y_{O_2} + D_{O_2,CO_2}Y_{N_2}$$
$$+ (D_{CO_2,N_2}Y_{CO_2}/r_{CO_2,O_2})\big]\ .$$

Values for the binary diffusion coefficients can be calculated from Table 1 (next section). For a temperature of $20\,^\circ C$ and a pressure of 101 kPa these values are 0.159×10^{-4}, 0.202×10^{-4}, and 0.159×10^{-4} (m^2/s) for D_{O_2,CO_2}, D_{O_2,N_2}, and D_{CO_2,N_2}, respectively. The Fickian diffusion coefficients can then be calculated if values for Y_{O_2}, Y_{CO_2}, Y_{N_2}, and r_{CO_2,O_2} are known. For example, with $Y_{O_2} = 0.15$, $Y_{CO_2} = 0.06$, $Y_{N_2} = 0.79$, and $r_{CO_2,O_2} = 0.5$, $D_{F_{O_2}}$ and $D_{F_{CO_2}}$ are calculated to be 0.210×10^{-4} and 0.150×10^{-4} m^2/s, respectively. These two points are indicated on Fig. 2 and 3 where the values of $D_{F_{O_2}}$ and $D_{F_{CO_2}}$ are plotted for various flux ratios. In both figures Y_{N_2} is held constant at 0.790 while Y_{O_2} varies from 0.0 to 0.21. Carbon dioxide comprises the remainder of the atmosphere $(0.21 \le Y_{CO_2} \le 0.0)$.

The apparent diffusion coefficients for both O_2 and CO_2 vary little for r_{CO_2,O_2} near 1.0. As the flux ratio deviates further from 1.0, the O_2 diffusion coefficient diverges rapidly as Y_{O_2} increases (Fig. 2). D_F for CO_2 is less variable but can deviate markedly from its value at $r_{CO_2,O_2} = 1.0$ at low values of the flux ratio and high CO_2 (low O_2) concentrations (Fig. 3). Values for the flux ratio in soils have been reported ranging between 0.6 and 4.0 (Bunt and Rovira, 1955; Rixon and Bridge, 1968; Bridge and Rixon, 1976). Although none of these authors reported the O_2 and CO_2 mole fractions at which these ratios were found, extreme values of 0.0 to 0.21 for O_2 and 0.0 and 0.09 for CO_2 have been measured (Russell and Appleyard, 1915). Using the values of 0.05 for Y_{CO_2} and 0.15 for Y_{O_2} and a flux ratio of 2.0, we can see from Fig. 2 and 3 that deviations in the Fickian diffusion coefficients of 15% for O_2 and 9% for CO_2 from the values at $r_{CO_2,O_2} = 1.0$ are possible. Figures 2 and 3 illustrate the potential hazard of applying values of the Fickian diffusion coefficient from one situation to another where the flux ratio and gas composition may not be the same. This may be, at least in part, the reason why flux calculations based

Table 1—Coefficients for calculating D_{ij}^{*}† for gas pairs of interest in soil research (after Marrero and Mason, 1972).

Gas couple	$a \times 10^7$	b	c	T range	Uncertainty‡ limits
	m^2 kPa s^{-1} K^{b-1}		K		%
Ar-CH$_4$	0.792	1.785	0.0	307–10^{-4}	3
Ar-N$_2$	0.913	1.752	0.0	244–10^4	2
Ar-O$_2$	0.987	1.736	0.0	243–10^4	3
Ar-air	0.926	1.749	0.0	244–10^4	3
Ar-CO$_2$	1.76	1.646	89.1	276–1800	3
CH$_4$-N$_2$	1.01	1.750	0.0	298–10^4	3
CH$_4$-O$_2$	1.68	1.695	44.2	294–10^4	3
CH$_4$-air	1.04	1.747	0.0	298–10^4	3
N$_2$-O$_2$	1.14	1.724	0.0	285–10^4	3
N$_2$-H$_2$O	0.188	2.072	0.0	282–373	4
N$_2$-CO$_2$	3.18	1.570	113.6	288–1800	2
O$_2$-H$_2$O	0.191	2.072	0.0	282–450	7
O$_2$-CO$_2$	1.58	1.661	61.3	287–1083	3
Air-H$_2$O	0.189	2.072	0.0	282–450	5
Air-CO$_2$	2.73	1.590	102.1	280–1800	3
H$_2$O-CO$_2$	9.33	1.500	307.9	296–1640	10
CO$_2$-N$_2$O	0.284	1.866	0.0	195–550	3

† $\ln(D_{ij}^{*}) = \ln(a) + b\ln(T) - c/T$, where T is temperature (K).
‡ Uncertainty in D_{ij}^{*} term at lower end of listed temperature range.

on concentration gradients do not compare well to other techniques for measuring flux (DeJong et al., 1979).

Equation [8] also applies to diffusion in four-component or greater gas mixtures. An O_2, CO_2, N_2, and Ar or O_2, CO_2, N_2, Ar, and H_2O vapor atmosphere would be mixtures of interest in soils. However, as in the ternary case, unless some simplifying assumptions can be made, the exact solution for diffusion in these mixtures is not possible.

BINARY DIFFUSION COEFFICIENT

D_{ij} is the proportionality coefficient relating the flux of i and j to their gradient in a binary gas system. Conceptually D_{ij} can be thought of as a macroscopic averaging of the interactions or collisions between components i and j. The greater the number of collisions, the more diffusion is impeded and the smaller D_{ij} must be. For this reason, D_{ij} must be inversely proportional to density, and thus pressure since the number of collisions will increase linearly with pressure at constant temperature. Thus

$$D_{ij} = D_{ij}^*/P , \qquad [26]$$

where D_{ij}^* is the temperature-dependent, pressure-independent binary diffusion coefficient. However, any decrease in D_{ij} due to a pressure increase will be exactly balanced by an increase in the number of molecules or flux carriers per volume of gas (increased concentration, C). This can be seen by substituting Eq. [26] into Eq. [9] for the flux in a binary system:

$$N_i = - \frac{D_{ij}^*/P}{1 - (1 - r_{ji})Y_i} \frac{P}{RT} dY_i/dz , \qquad [27]$$

the pressure terms drop out and the diffusion equation is pressure-independent when expressed in mole fractions:

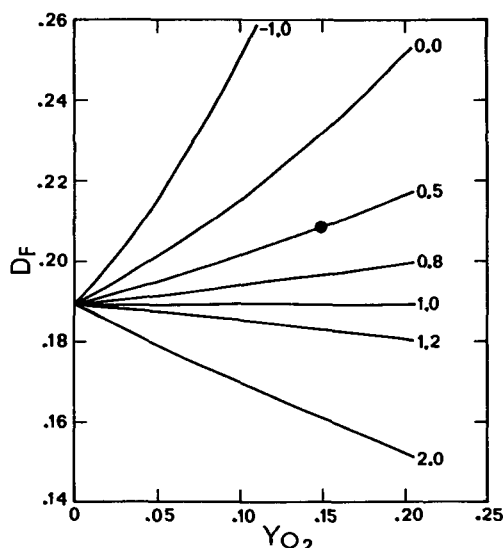$$N_i = - \frac{D_{ij}^*}{1 - (1 - r_{ji})Y_i} \frac{1}{RT} \frac{dY_i}{dz} . \qquad [28]$$

When working with the concentration form of the diffusion equation (Eq. [1]), the pressure dependence of the diffusion coefficient must be retained:

$$q_i = - \frac{D_{ij}}{1 - (1 - r_{ij})Y_i} \frac{P_1}{P_2} dC_i/dz , \qquad [29]$$

where P_1 is the total pressure at which D_{ij} is known and P_2 is the pressure at which diffusion is taking place.

Relations for calculating D_{ij}^* for any gas pair, based on classical statistical mechanics, were independently developed by Chapman and by Enskog (Chapman and Cowling, 1939). The solution involves successive approximations to D_{ij}^*. The approximations converge rapidly, so that the first approximation, which is temperature-dependent but independent of gas composition and at most the second approximation, which introduces slight compositional variation, is sufficient for calculating D_{ij}^* to within at most several percent error (Marrero and Mason, 1972).

Values for D_{ij}^* (more commonly D_{ij}), can be found in numerous papers in the literature (see Marrero and Mason, 1972), with some recent values for carbon dioxide, nitrous oxide, ethylene, and ethane presented by Pritchard and Currie (1982). Marrero and Mason (1972) have compiled an extensive tabulation of binary diffusion coefficients taken from the literature. Based on the Chapman–Enskog equations and extensive experimental results, they have compiled semiempirical relations for the first approximation of over 70 gas pairs. Diffusion coefficients for gas pairs of interest in soil research are tabulated in Table 1. In all cases shown, the second approximation to D_{ij}^*, which is based on the compositional ratio of component i to component j, represents a correction to the first approximation of $< 1.0\%$ at normal temperatures for the entire compositional range. This correction is within the experimental error of the measured values and can be neglected for all the gas pairs listed. The equation used by Marrero and Mason (1972) to calculate D_{ij}^* is

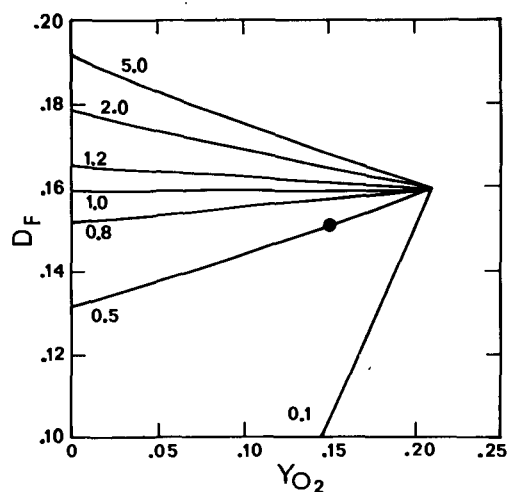$$\ln(D_{ij}^*) = \ln(a) + b\ln(T) - c/T. \qquad [30]$$

Fig. 2—Fickian diffusion coefficient, D_F, (m^2 s^{-1}) for O_2 in an O_2–CO_2–N_2 atmosphere vs. mole fraction of O_2. Plot is for 20°C and 101 kPa with $N_{N2} = 0.0$, $Y_{N2} = 0.790$, and $Y_{CO2} = 0.21 - Y_{O2}$. Curve labels are the flux ratio $r_{CO2,O2}$. Point shows value calculated in text.

Fig. 3—Fickian diffusion coefficient, D_F, (m^2 s^{-1}) for CO_2 in an O_2–CO_2–N_2 atmosphere vs. mole fraction of O_2. Plot is for 20°C and 101 kPa with $N_{N2} = 0.0$, $Y_{N2} = 0.790$, and $Y_{CO2} = 0.21 - Y_{O2}$. Curve labels are the flux ratio $r_{CO2,O2}$. Point shows value calculated in text.

They computed the constants a, b, and c by matching Eq. [30], whose form is suggested by the theoretical work of Chapman–Enskog, to a compilation of experimental data for each gas pair. The temperature range over which these coefficients were fit and the uncertainty limits in D_{ij}^* at the lower end of the temperature range are also given in Table 1.

An example calculation of D_{ij}^* using values in Table 1 is as follows. The pressure-independent, diffusion coefficient for the gas pair O_2–CO_2 is calculated from Eq. [30] with the coefficients from Table 1 of $a = 1.58 \times 10^{-7}$, $b = 1.661$, and $c = 61.3$. At a temperature of 293 K,

$$\ln(D_{O_2,CO_2}^*) = \ln(1.58 \times 10^{-7}) + 1.661 \ln(293.)$$
$$- 61.3/293 . \qquad [31]$$

$$D_{O_2,CO_2}^* = 0.00160 \ \text{m}^2 \ \text{kPa} \ \text{s}^{-1} ,$$

or at atmospheric pressure, from Eq. [26],

$$D_{O_2,CO_2} = 0.00160/101$$

$$= 0.159 \times 10^{-4} \text{m}^2/\text{s} . \qquad [32]$$

The diffusion coefficients are highly sensitive to temperature with a 30% variation possible under normal, seasonal soil temperature fluctuations. For example, the binary diffusion coefficient for the O_2–CO_2 gas pair is equal to 0.136×10^{-4} at $0°C$ (273 K) and 0.165×10^{-4} at $30°C$ (303 K) or $D_{O2,CO2}$ is 22% greater at $30°C$ than $0°C$.

SUMMARY

The comparison of the Stefan–Maxwell equations and Fick's Law for diffusion of gas through vapor shows that only under certain, special circumstances is the diffusion coefficient for Fick's Law, D_{Fi}, a constant independent of the mole fraction of i and the diffusion flux of other gases. These special cases are the diffusion of a trace amount of component i, in a multicomponent gas mixture, equimolar, counter-current diffusion in a binary gas mixture, and equimolar, counter-current diffusion of two gases in a ternary system with the third gas stagnant. In general, D_{Fi} is dependent on the binary diffusion coefficients, the composition of the gas mixture, and the diffusional flux ratios of the gas components. Measured values of D_{Fi} can only be accurately extrapolated to other circumstances when all the above conditions are similar. In an O_2, CO_2, and N_2 atmosphere where N_2 is stagnant, variations on the order of 10% from the tracer value of D_F for O_2 and CO_2 are possible with variations in the mole fraction, or flux ratio. The diffusion coefficients are most sensitive to changes in the flux ratio for ratios < 0.8 or > 1.2. The temperature- and pressure-dependent nature of the diffusion coefficient must also be considered.

APPENDIX

a, b, c = semiempirical constants
C_i = concentration of gas component i, kg m^{-3}
$\bar{v}_i$, $\bar{v}_j$ = average velocity of gas i and j respectively, m s^{-1}
D_{Fi} = Fickian diffusion coefficient for component i, m^2 s^{-1}
D_{ij} = binary diffusion coefficient, m^2 s^{-1}
D_{ij}^* = temperature-dependent, pressure-independent binary diffusion coefficient, kPa m^2 s^{-1}
D_T = coefficient of thermal diffusion, m^2 s^{-1}
F_i,F_j = external force field acting on gas i and j, N/kg
m_i,m_j = mass of molecules of gas i and j, respectively, kg

M_o = Avagadro's number, mol^{-1}
n_i,n_j = number density of gas i and j respectively, m^{-3}
$n_T = n_i + n_j$
N_i = molar flux of gas i, mol m^{-2} s^{-1}
P = total pressure, kPa
q_i = mass flux of gas i, kg m^{-2} s^{-1}
r = direction vector, m
R = universal gas constant, m^3 kPa mol^{-1} K^{-1}
r_{ji} = flux ratio, $-N_j/N_i$
t = time, s
T = absolute temperature, K
Y_i = mole fraction of component i
z = distance or depth, m
α = combined air-filled porosity, tortuosity term
Π = product operator
ρ_i,ρ_j,ρ_T = density of gas i, j, and the combined gas density respectively, kg m^{-3}
Σ = summation operator

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