Gaseous Diffusion in the Leaf Interior

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ABSTRACT

A one dimensional, steady state, constant temperature model of gaseous diffusion in the leaf interior is presented. The model is shown to predict that CO₂ is absorbed into mesophyll cell walls generally throughout the deep interior of the leaf, while water vapor essentially evaporates only from those cell walls near the substomatal cavity.

INTRODUCTION

When the stomata of a leaf are open, there is a diffusive flow of gases between the leaf interior and the air outside the leaf. Water vapor, during the process of transpiration, evaporates from the mesophyll cell walls and diffuses through the intercellular air pathway to the substomatal cavity, and then through the stomatal pore to the leaf exterior. On the other hand, CO₂ used by the mesophyll cells in photosynthesis, diffuses in the opposite direction: from the leaf exterior, through the stomatal pore and into the intercellular air pathway. Gaseous CO₂ is finally absorbed into the mesophyll cell walls and CO₂ proceeds as a diffusing solute to the chloroplasts in the cell interior. The diffusive path for gaseous CO₂ is thought to be considerably longer than the comparable path for water vapor (Meidner, 1975; Aston and Jones, 1976).

This work presents a mathematical model of gaseous diffusion in the intercellular air pathway. The model includes diffusion from the mesophyll cell walls which line the air pathway (corresponding to evaporation or absorption), as well as diffusion along the length of the pathway. This provides a more realistic description of the movement of gases within the leaf than the usual resistance model which omits diffusion from the pathway walls (Meidner and Mansfield, 1968; Nobel 1974).

The model is shown to predict that CO₂ is absorbed into mesophyll cell walls generally throughout the deep interior of the leaf, while water vapor essentially evaporates only from those cell walls near the substomatal cavity. As Meidner (1975) has noted, "This fits the primary function of these walls, namely to offer a moist surface for the absorption of carbon dioxide rather than for evaporation."

THE MODEL

The intercellular air pathway is modeled as a cylindrical tube of circular cross-section. (It should be noted, however, that the analysis is easily generalized to apply to a cylinder of arbitrary cross-section, without changing the nature of the conclusions.) The model is one dimensional, steady state and of constant temperature. The actual situation in the leaf interior is, of course, of much greater complexity than that of such a simplified model (Fig. 1); nevertheless, it is believed that the conclusions drawn from this model are qualitatively applicable to the real leaf.

Let x represent the distance along the pathway of total length L, i.e., 0 ≤ x ≤ L. The boundary x = O represents the leaf interior while the boundary x = L represents the substomatal cavity (Fig. 2).

Let C₁(x) and C₂(x) represent the concentrations [g/cm³] of water vapor and gaseous CO₂, respectively, at the centerline of the air pathway, at cross-section x. Although C₁ actually varies across the cross-section, the value of C₁ at cross-section x will be identified with C₁(x), the value at the centerline.

The following boundary conditions on C₁(x) and C₂(x) are assumed:

At x = O there is no flux,

\[ J₁ = -D₁ \frac{dC₁}{dx} = 0, \quad x = 0 \]

\[ C₁ = \tilde{C}_₁ \]

FIG. 1 Transverse section of a leaf [after Nobel, 1974, p. 3].

FIG. 2 One dimensional model of an intercellular air pathway.
where
\[ J_1 = \text{diffusive flux, g/cm}^2\text{s} \]
\[ D_I = \text{diffusion coefficient in air, cm}^2/\text{s} \]
and where subscripts 1 and 2 again refer to water vapor and gaseous CO₂, respectively. Here \( x = 0 \) represents either a physical boundary (e.g. a “dead end”), or a plane of symmetry such that at cross-sections located at \( x = O^+ \) and \( x = O^- \) the flow proceeds in opposite directions along the length of the pathway.

At \( x = L \) the concentration is assumed constant,
\[ C_l = C^* \quad x = L \] [2]

Here \( C_l \), the concentration of gas i in the substomatal cavity, is viewed as being given. (Actually \( C_l \) depends upon the concentration of gas i in the atmosphere outside the leaf as well as upon other parameters, e.g. resistances. By assuming that \( C_l \) is given, the air pathway problem becomes uncoupled from that of the flow in the stomatal pore in the leaf exterior.)

It is assumed that the evaporation of water vapor from, and the absorption of CO₂ into the walls of the pathway are governed by the following expression for flux \( E_i \)(g/cm²/s)
\[ E_i = H_i (C_i^* - C_i) \] [3]

where
\[ C_i = C_i(x) = \text{concentration of gas i at the centerline of the air pathway, at cross-section x} \]
\[ C_i^* = C_i^*(x) = \text{concentration of gas i at the wall of the air pathway, at cross-section x} \]

and where
\[ H_i = D_i / R \] [4]

where \( R \) = radius of pathway cross-section. Here \( E_i > 0 \) for water to evaporate from the walls into the pathway, while \( E_i < 0 \) for CO₂ to be absorbed into the walls. Equation [3], which models evaporation and absorption as diffusion processes, has been found to be applicable to the case of evaporation from open bodies of water in still air (Marciano and Harbeck, 1954, p. 61). (In the literature of heat transfer (also a diffusive process), equation [3] represents a “radiation” condition (Carslaw and Jaeger, 1959, p. 134).

The expression [4] for the proportionality constant \( H_i \) (“surface conductance” in heat transfer) results from consideration of the resistance associated with the diffusive flux of gas i between the centerline of the pathway and the pathway wall. By definition, (Nobel, 1974, p. 304)
\[ \text{resistance} = \text{concentration difference/flux} = \text{distance diffused/diffusion coefficient}. \]

Using equation [3] and taking R as the distance diffused, find that resistance = \( 1 / H_i = R / D_i \).

Now consider a volume element \( \Sigma \) of length \( dx \) and having the circular cross-section of the pathway. The rate [g/s] at which mass is added to \( \Sigma \) due to the flux \( E_i \) is \( (2\pi R dx) E_i \). For mass to be conserved this must be balanced by the rate at which mass is lost from \( \Sigma \) due to diffusion, \( (\pi R^2 dx)(D_i/dx) \). Equating these rates and using equation [3] gives
\[ d^2 C_i / dx^2 + 2 \pi R^2 (C_i^* - C_i) = 0 \] [5]

Equation [5] with the boundary conditions (1) and (2) must be satisfied by both water vapor and CO₂; thus far the derivation is the same for both. When considering the quantity \( C_i^* \), however, the two gases receive separate treatment.

The gas concentration \( C_i^* \) at the pathway wall is assumed to result from equilibrium of the gas i with the liquid in the mesophyll cell walls. (The mesophyll cells are assumed to be distributed uniformly around the walls of the pathway.) Assuming the cell wall liquid is a dilute aqueous solution, water will play the role of the solvent and CO₂ the solute.

The gas concentration \( C_1^* \) of the solvent (water) is governed by Raoult’s law (Merva, 1974, p. 248; Nobel 1974, p. 459),
\[ C_1^* = c_1_{sat} N_1 \] [6]

where
\[ C_1_{sat} = \text{saturation value of } C_1 \text{ in air at assumed (constant) temperature.} \]
\[ N_1 = \text{mole fraction of water in cell wall liquid.} \]
For a dilute solution, \( N_1 \approx 1 \). This leads to the assumption that (Slatyer, 1967, p. 258)
\[ C_1^* = c_1_{sat} = \text{constant} \] [7]

The gas concentration \( C_2^* \) of the solute (CO₂) is governed by Henry’s law (Nobel, 1974, p. 459),
\[ C_2^* = K N_2 \] [8]

where
\[ K = \text{a proportionality constant (temperature dependent)} \]
\[ N_2 = \text{mole fraction of CO}_2 \text{ in cell wall liquid.} \]
At typical leaf temperatures, evaluation of Henry’s Law shows that (Nobel, 1974, p. 330)
\[ C_2^* = c_2_{liq} \] [9]

where \( C_{2_{liq}} = C_{2_{liq}}(x) = \text{concentration of CO}_2 \text{ in cell wall liquid.} \)
In order to establish a more convenient expression for \( C_2^* \), the conservation of mass is applied to the \( CO_2 \) absorption process: The flux of gaseous \( CO_2 \) from the pathway into the pathway wall equals the flux of dissolved \( CO_2 \) from the mesophyll cell walls into the chloroplasts. This latter flux is proportional to the difference in \( CO_2 \) concentration between cell wall and chloroplast (Nobel, 1974, pp. 325-340.) Assuming that the \( CO_2 \) concentration in the chloroplasts is zero (Monteith 1963, p. 98), the flux of dissolved \( CO_2 \) becomes \( C_2 liq/\Omega \), where \( \Omega \) is the resistance associated with this flux.

Using equations [3], [4] conservation of mass requires

\[
\frac{D_2 (C_2 - C_2^*)}{R} = \frac{C_2 liq}{\Omega} \hspace{2cm} [10]
\]

Eliminating \( C_2 liq \) from equations [9], [10], find

\[
C_2^* = (1+\alpha^2)^{-1} C_2 \hspace{2cm} [11]
\]

where

\[
\alpha^2 = \frac{R}{D_2 \Omega} \hspace{2cm} [12]
\]

As noted above, \( R/D_2 \) is the resistance associated with the \( CO_2 \) vapor flux from the centerline of the pathway to the wall. Thus the parameter \( \alpha^2 \) is the ratio of two resistances encountered by diffusing \( CO_2 \). For typical values of \( R, \Omega, D_2 \), the parameter \( \alpha^2 \ll 1 \). E.g., with \( R = 5 \mu m, \Omega = 6 \text{sec/cm} \) (Nobel, 1974, p. 340), and \( D_2 = 0.16 \text{cm}^2/\text{sec} \), obtain \( \alpha = 0.023 \). Application of the binomial expansion to equation [11] gives

\[
C_2^* = (1-\alpha^2) C_2 \cdot \alpha^2 \ll 1 \hspace{2cm} [13]
\]

Now the expressions for \( C_1^* \) and \( C_2^* \) (equations [7] and [13]) are substituted into the governing equation [5], giving

\[
\text{water vapor: } \frac{d^2 C_1}{dx^2} + \frac{2}{R^2} (C_{sat} - C_1) = 0 \hspace{2cm} [14]
\]

\[
\text{CO}_2: \frac{d^2 C_2}{dx^2} - \frac{2 \alpha^2}{R^2} C_2 = 0 \hspace{2cm} [15]
\]

Equations [14], [15] together with the boundary conditions (1), (2) possess the following solutions

\[
\text{water vapor: } C_1(x) = C_{1 sat} + (\hat{C}_1 - C_{1 sat}) \cosh \frac{x}{L} \hspace{2cm} [16]
\]

\[
\text{CO}_2: \frac{\cosh \frac{x}{L}}{\cosh \frac{L}{\lambda}} \hspace{2cm} [17]
\]

where

\[
\lambda = \sqrt{\frac{2 L}{R}} \hspace{2cm} [18]
\]

and where \( \hat{C}_1, \hat{C}_2 \) are the gas concentrations in the substomatal cavity, \( x = L \) (equation [2]).

Jarvis and Slatyer (1970), p. 310, state that anatomical examination of cotton plants (\( Gossypium hirsutum \)) revealed that \( R \) varied from 0 to 7.2 \( \mu m \) while \( L \) was about 200 \( \mu m \). Taking \( R = 5 \mu m \) and \( L = 200 \mu m \), the parameter \( \lambda = 57 \). Equations [16] and [17] are displayed in dimensionless form in Fig. 3 for \( \lambda = 57 \) and \( \alpha = 0.023 \).

Discussion

Note from Fig. 3 that the solution for \( C_1(x) \) shows that the evaporative flux of water vapor from the pathway walls, \( E_1 \), occurs chiefly near the substomatal cavity end of the pathway, \( x = L \). (From equations [3] and [7] it follows that \( E_1 \) is proportional to \( C_{sat} - C_1(x)/(C_{sat} - \hat{C}_1) \) of Fig. 3). Comparison with \( C_2(x) \) shows that the absorptive \( CO_2 \) flux, \( E_2 \), occurs significantly all along the length of the pathway. (Equations [3] and [13] reveal that \( E_2 \) is proportional to \( C_2(x)/C_2 \) of Fig. 3).

In order to quantify this observation, define a position along the pathway \( P_1 \) such that the length of pathway \( P_1 \leq x \leq L \) is responsible for, say 90 percent of the total flux \( E_1 \) through the pathway wall. Then \( P_1 \) satisfies the following condition:

\[
\int_{0.9}^{1} E_1(x) \, dx = \int_{0}^{P_1} E_1(x) \, dx \hspace{2cm} [19]
\]
For water vapor \( (i = 1) \), equations [3], [7], [16] yield after substitution into equation [19],

\[
\sinh \frac{\lambda P_1}{L} = 0.1 \sinh \lambda \quad \ldots \quad [20]
\]

Again using \( \lambda = 57 \), equation [20] gives

\[
P_1 = 0.96L \quad \ldots \quad [21]
\]

For \( \text{CO}_2 \) \( (i = 2) \), equations [3], [13], [17] yield after substitution into equation [19],

\[
\sinh \frac{\lambda a P_2}{L} = 0.1 \sinh \lambda a \quad \ldots \quad [22]
\]

With \( \lambda = 57, a = 0.023 \), equation [22] gives

\[
P_2 = 0.13L \quad \ldots \quad [23]
\]

Equations [21], [23] reveal that while 90 percent of all water vapor evaporation occurs within the first 4 percent of the pathway near the substomatal cavity, 87 percent of the pathway is required for 90 percent of all \( \text{CO}_2 \) absorption.

It is important to note that the qualitative nature of these results remains unchanged for a wide range of geometrical parameters \( R \) and \( L \). Specifically, if \( \lambda = \sqrt{2} \frac{L}{R} \gg 1 \) (i.e. if the pathway length is much larger than the pathway radius) and if \( a = (R/D_2Q)^{1/2} \ll 1 \) (i.e. if the resistance of \( \text{CO}_2 \) diffusing as a solute from cell wall to chloroplast is much larger than the resistance encountered by gaseous \( \text{CO}_2 \) diffusing from the centerline of the pathway to the pathway wall), while \( \lambda a \approx 1 \), then \( P_1 \) and \( P_2 \) attain values comparable to those presented above.

CONCLUSION

A mathematical model of the gaseous diffusion of \( \text{CO}_2 \) and of water vapor in an intercellular air pathway of a leaf has been presented. The mathematical treatment of these gases differs because \( \text{CO}_2 \) (considered as a solute in the cell wall liquid) obeys Henry's law, while water vapor (associated with the solvent) follows Raoult's law.

The model predicts that \( \text{CO}_2 \) is absorbed into mesophyll cell walls generally throughout the deep interior of the leaf, while water vapor essentially evaporates only from those cell walls near the substomatal cavity. This conclusion agrees with the recent experimental work of Meidner (1975) and Aston and Jones (1976).

References