5 The theory of gas diffusion through stomata

5.1 Introduction

Over the last century our understanding of gas exchange between a leaf and its environment has increased greatly from the use of simple concepts of resistance to diffusion (e.g. Brown and Escombe, 1900) to the development of complex models and theory (see, e.g. Penman and Schofield, 1951; Monteith, 1983). Although the general concepts are now well established (see, e.g. Weyers and Meidner, 1990; Nobel, 1991; Jones, 1992) some controversial aspects, such as the diffusion of gases inside leaves (see, e.g. Parkhurst, 1994), remain. In this section, emphasis will be on the theory of diffusion of gases through stomata. The various techniques for measuring stomatal resistance, or its reciprocal, stomatal conductance, have been extensively covered elsewhere (see, e.g. Sestak et al., 1971; Weyers and Meidner, 1990).

Leaves are the major organs of gas exchange in plants (with the exception of many submerged aquatic ones) and their surfaces are cuticularized to varying degrees. The cuticle is relatively impermeable to gases including water vapour and CO$_2$. Thus gas exchange is mainly governed by stomatal aperture and the distribution of stomata in the surface of the leaf. Normally when a leaf is photosynthesizing, the stomata are open and there will be a net movement of CO$_2$ into and water vapour and oxygen out of a leaf. Partial closure of stomata will have a larger relative effect on water vapour loss than CO$_2$ uptake, mainly because the diffusion pathway for CO$_2$ is longer than that for water vapour. Stomatal restriction is therefore a smaller proportion of the total impedance for carbon dioxide fluxes. However, at very small apertures a relatively high efflux of water vapour may retard CO$_2$ influx.

5.2 Fick's law and the driving forces for diffusion

The flux of CO$_2$ into or water vapour out of a leaf depends largely on two quantities, i.e. the driving forces for movement and the resistances
encountered en route. The driving forces for diffusion through the stomata are determined by the difference in free energy of the molecules in the atmosphere and the substomatal cavity. For gases at a constant temperature, the free energy is related primarily to the number of molecules present per unit volume (molar concentration) or the mass of gas per unit volume (mass concentration). Thus Fick’s law states that the rate of mass transfer \( J \) is directly related to the concentration gradient \( \partial c / \partial x \) by a constant termed the diffusion coefficient \( D \)

\[
J = -D \frac{\partial c}{\partial x}
\]  

(5.1)

Where \( J \) is the rate of mass transfer \( (g \ m^{-2} \ s^{-1}) \), \( D \) is the diffusion coefficient \( (m^2 \ s^{-1}) \) and \( \partial c / \partial x \) is the concentration (or density) gradient of the gas \( (g \ m^{-3}) \). The minus sign associated with \( D \) in equation (5.1) indicates diffusion occurs towards the region of lower concentration. The diffusion coefficient, \( D \), is not strictly constant, but is affected by gas concentration, temperature, pressure and the molecular weight of the gas (from Graham’s law which states that the relative rates of diffusion of two gases are inversely proportional to the square root of their densities or molecular weights). The diffusion coefficient is effectively constant at a fixed temperature and pressure if the changes of gas concentration across the tube (pore) are negligible, which is the case for \( CO_2 \). Thus at 20°C and atmospheric pressure \( (0.1013 \ MPa) \), \( D_{CO_2} \) in air is \( 15.1 \ mm^2 \ s^{-1} \) and \( D_{wv} \) for saturated water vapour is \( 242 \ mm^2 \ s^{-1} \). Cowan and Milthorpe (1968) suggest that the diffusion coefficient for water vapour in free air should be reduced when considering flux through a stomatal pore to take into account molecular interactions of water with the pore walls, thus the value of \( D_{wv} \) should be reduced as the pores become smaller.

In the case of water vapour, the various measurements of concentration have particular terms. Absolute humidity corresponds to the mass or number of molecules per unit volume \( (i.e. \ equivalent \ to \ c \ in \ equation \ 5.1) \). The maximum value of the absolute humidity for water vapour in equilibrium with pure water is termed the saturation concentration of water vapour in air, which increases markedly with temperature (Fig 5.1) As the air is often not saturated with water vapour, relative humidity expresses the absolute humidity as a percentage of this maximum saturation value for a given temperature. However, as the leaf temperature is often higher than the air temperature due to absorption of radiant energy, the same concentration of water vapour would correspond to a different relative humidity at each location. Thus it is usual to express concentrations in terms of partial pressures or mole fractions which explicitly include a temperature term. The absolute humidity is related to the partial pressure of water vapour \( (e) \) as follows

\[
c = \frac{e M}{RT}
\]  

(5.2)