6 Figures, 4 Appendices, 1 Highlighted Box (with 1 figures), 3 Footnotes

Chapter 5. Diffusion, Continuity, Energy Budgets and Water Transport

…the experimental information we possess on the subject amounts to little more than the well established fact, that gases of different nature, when brought into contact, do not arrange themselves according to their density, the heaviest undermost, and the lighter uppermost, but they spontaneously diffuse, mutually and equally, through each other, and so remain in the intimate state of mixture for any length of time.

Thomas Graham (1833)

…according to the molecular kinetic theory of heat, bodies of a microscopically visible size suspended in liquids must, as a result of thermal molecular motions, perform motions of such magnitudes that they can be easily observed with a microscope.

Albert Einstein (1905)

The observation that a mixture of gas molecules of different masses does not behave as expected when subjected to the force of gravity, was systematically described by Thomas Graham early in the 19th Century. Rather than sorting according to their masses, with the heavier molecules accumulating at the bottom of a vessel, Graham observed that a true mixture was maintained over time. It was clear that a force must exist to oppose gravity and facilitate the intermingling of gases; but, what could be nature of such a force? Even earlier, in 1827, Robert Brown had observed that pollen grains suspended in water and observed under a microscope exhibited random patterns of motion. He reasoned that these motions must be caused by randomly arranged forces; but once again, the nature of such forces was not evident. It wasn't until several decades later that Albert Einstein, working on issues concerned with heat and kinetic energy, provided a theoretical explanation. Einstein reasoned that the thermal heat contained within a body is potentially transformed into kinetic energy, providing a means for motion. In the case of Graham's gases, we can use Einstein's theory to explain how suspended molecules can move upward, in apparent defiance of gravity; thus, mixing molecules randomly. In the case of Brown's pollen grains, we can use the theory to explain the perpetual motion of water molecules, with consequent random collisions between molecules and grains. Following the tenets of Newtonian physics, motion requires a force. In fact in Newtonian terms, a force is identified as the product between mass and acceleration. It's acceleration under an appropriate force that reflects the movement of mass from a state of no velocity to a state of velocity. At the scale of molecules, the movement of mass is known as diffusion.

As we continue our discussions of the forces underlying the exchange of mass and energy within the earth system, and between plants and the atmosphere, we will take some time to understand the basis for molecular diffusion. Diffusion is driven ultimately by molecular collision. The force of one molecule colliding with another, and the associated kinetic motion that it causes, is clearly restricted to fairly short distances. Over time, the collective activity of molecular collisions can potentially drive an enormous number of molecules from one point to another, but it should be obvious that even this form of 'collective diffusion' is limited to relatively short distances.

We begin this chapter with a discussion of diffusion as a process, focusing on its dependence on gradients in molecular collision. We will make the point that while we understand much about the mechanisms and forces that cause diffusion, when it comes to modeling the process we revert to simple statistical predictions based on assumptions of linearity and Gaussian patterns of variance. Following a discussion of diffusion in principle, we will consider the specific case of diffusion through porous media. This latter discussion will set the stage for treatments in later chapters where we consider the specific cases of diffusion through soil and through the stomata of plant leaves. Following the discussion of diffusion through pores, we will take note of a fundamental mathematical relationship that emerges from diffusion theory; the linkage between a change in flux across space and a change in concentration across time. This linkage is required by the conservation of mass and establishes one of the most fundamental relationships in flux theory; the concept of continuity. Continuity provides the foundation for concepts such as mass balance and conservation of mass and momentum which, once again, will be central in our future discussions of fluxes between ecosystems and the atmosphere. Finally, in order to lay the foundation for our discussion on water fluxes through plants, we will take up the issue of osmosis, a special case of diffusion, and the concept of water potential, the thermodynamic basis by which water does work in plants, including the transport of nutrients and the movement of energy as latent heat.

5.A Diffusion

Diffusion is a process of particle movement and collision. Movement is propelled by the internal heat content of the particles; as heat is converted into kinetic energy, particles move. A collection of particles moving in random directions will tend to collide with one another. The frequency of collision will depend on the density of the particles. The energy of impact in the collisions will depend on the kinetic energy carried by the particles, which in turn determines their speed of movement between collisions. As a molecule diffuses through a fluid, colliding with other molecules and being forced into new locations, a process of mutual displacement occurs; with molecules continually exchanging places with one another. On average, diffusion occurs through *binary exchange*; the process whereby one molecule exchanges places with another, such that the 'center of mass' of the fluid remains constant. The concept of binary exchange carries the implicit assumption that *bulk flow does not occur*; that is, that the fluid that contains the diffusing entity does not have a velocity that advects the entity from one point to another; the fluid is 'still'.

5.A.1. Diffusion time and space scales

Diffusion can be characterized by characteristic length and time scales. It's important to understand these scales in order to gain some perspective about the constraints on diffusion as a transport process. The *mean free path* is defined as the average distance covered by a diffusing particle before it makes contact with another particle (either of the same or different type) or with the walls of the diffusion vessel, and *mean free time* is the average time between contacts. The mean free path and speed of particle movement are principal determinants over the rate of diffusion, and are reflected in the term *diffusivity*. Diffusivity describes the inherent capacity for diffusion in a system when normalized by the concentration gradient. Diffusivity is described with units of $m^2\ s^{-1}$. Upon inspection of these units, it's clear that diffusivity can be viewed as the product between a velocity ($m\ s^{-1}$) and distance (m). As diffusion is fundamentally propelled by particle movement and resisted by particle collision, diffusivity is determined by the velocity of particles in time intervals between contacts; in other words, diffusivity reflects the product between free flight velocity and mean free path.

Diffusivity is influenced by the medium through which particles diffuse. The diffusivity of

CO_2 molecules in air, for example, is 10,000 times higher than that for CO_2 in water (16 mm^2 s^{-1} in air compared to 0.0016 mm^2 s^{-1} in water). At a constant temperature, the average kinetic energies of CO_2 molecules in air versus water are constant; meaning that free flight velocity should also be constant. Thus, the lower diffusivity of CO_2 in water versus air must be due to a lower mean free path in water, which in turn reflects the higher density of molecules in water. The high frequency of contacts between CO_2 molecules and H_2O molecules in water reduces the mean free path, and concomitantly, the diffusivity of CO_2.

Using the concept of diffusivity, and applying it across a standard unit of time, we can develop a one-dimensional perspective on the effective distances involved in diffusive transport. *Diffusion length* describes the distance that a defined density of constituent is propagated in a given amount of time. Mathematically, the diffusion length is defined as $2\sqrt{K_d t}$, where K_d is the diffusivity (or more formally, the molecular diffusion coefficient). In order to provide an example, let's return to our case of CO_2 diffusing in air versus water. The diffusivity of CO_2 molecules in air is 16 mm^2 s^{-1}. Using a time scale of 1 second (an approximate time scale for leaf-atmosphere exchange), the diffusion length is estimated to be 8 mm. In water, the diffusivity of CO_2 is 0.0016 mm^2 s^{-1}. The diffusion length is calculated as 0.08 mm. Thus, as a transport process, diffusion is most effective at distances of a few millimeters or less; distances that characterize transport through a cell or across a leaf epidermis. Using diffusion length, we see that the downward transport of CO_2 from the atmosphere into a photosynthesizing canopy has relatively limited potential if attributed to diffusion alone; over 12 hours, a unit density of CO_2 can only be transported 0.68 m by diffusion alone.

5.A.2 Fick's diffusion model

"…according to this law [Graham's Law], the transfer of salt and water occurring in a unit of time between two elements of space filled with two different solutions of the same salt, must be, ceteris partibus, directly proportional to the difference of concentrations, and inversely proportional to the distance of the elements from one another".

Adolph Fick (1855)

Now let's link the physical basis for diffusion with a mathematical framework capable of predicting the direction and rate of diffusive flux. The directional vector along which a population of molecules is most likely to move can be described in terms of a statistical probability. When the density of molecules is greater in one region compared to a neighboring region, there is a greater probability that random motions will drive more molecules from the region of higher density toward the region of lower density, than vice versa. Statistical probability provides the basis for modeling diffusion. In the middle of the nineteenth century, Adolf Fick, a German physiologist, conducted studies on diffusion that led to a quantitative model that bears his name. Fick's model is based on a linear probability function that, in its most basic terms, relates diffusive flux (F) to diffusivity (K_d), difference in concentration between two points (Δc), and distance between the two points (Δx); when stated within the limit as $\Delta x \to 0$ the concentration gradient is expressed as $\partial c/\partial x$:

$$\mathrm{F} = -K_d\left(\frac{\partial \mathrm{c}}{\partial x}\right) \qquad (5.1)$$

where F is expressed in units of mol m^{-2} s^{-1}, when K_d is in units of m^2 s^{-1}, c is expressed as mol m^{-3}, and x is in m. The negative sign on the right side of the equation indicates the direction of net flux; i.e., from higher concentration toward lower concentration, which is opposite the direction in which the gradient increases. Equation 5.1 is commonly referred to as *Fick's first law of diffusion*.

The underlying driving force in Fick's first law is a concentration gradient. Clearly concentration does not, by first principles, represent a 'force', in the Newtonian sense of the term. Fick's law actually uses the gradient in *molecule concentration* as a convenience to reflect the gradient in *molecule collision concentration*, which in fact provides the driving force. In practical usage, the Fickian concentration gradient ($\partial c/\partial x$) is expressed in terms of different units. One of the most commonly-used expressions for $\partial c/\partial x$ has c in terms of *density* (moles or mass per unit volume). For gases, density is dependent on pressure and temperature and defined by the ideal gas law (see Section 2.D). In other cases, particularly in the atmospheric sciences, c may be expressed as *mixing ratio*, defined as the mass or volume of a single constituent per unit mass or volume of total constituents (i.e., g g^{-1} or m^3 m^{-3}). In the biological sciences, c is often expressed as *mole fraction*, defined as the molar fraction of a single constituent per mole of all constituents (i.e., mol mol^{-1}). Finally, particularly when discussing the diffusion of gases, c may be expressed in terms of *partial pressure*, defined as the pressure (with units Pa) created by a single gas constituent when present in a mixture of several constituents. Mixing ratio and mole fraction *are not* dependent on pressure and temperature. Density and partial pressure *are* dependent on pressure and temperature. The mixing ratio or mole fraction [represented as c(m)], and partial pressure (represented as p), can be related to density [c(d)] according to:

$$\mathrm{c(d)} = \mathrm{c(m)}\left(\frac{\mathrm{P}}{R\mathrm{T}}\right) = \frac{\mathrm{p}}{R\mathrm{T}} \qquad (5.2)$$

The dependence of density and partial pressure on atmospheric pressure causes potential diffusive limitations to the photosynthetic processes of leaves as elevation increases. The distributional range of many plant species extends from lower to higher elevations, forcing their photosynthetic systems to assimilate atmospheric CO_2 at progressively decreasing densities as they migrate up mountainous terrain. At the lower atmospheric CO_2 densities, CO_2 will potentially diffuse more slowly into the chloroplasts of plants, thus limiting the ultimate rate of CO_2 assimilation. This relation has led to the hypothesis that plants native to high elevations possess biochemical or physiological adaptations to compensate for the reduced availability of CO_2. Diffusive limitations are relieved to some extent, however, by the fact that K_d, the diffusion coefficient for CO_2 is increased at the lower atmospheric pressures of high elevation. A theoretical examination of the diffusive relations of plants as a function of altitude provides students with a useful case study on the connections between diffusion and metabolism; accordingly, we have presented a treatment of such a case study in Box 5.1.

5.B Diffusion across porous surfaces

Much of what we will discuss in the next two chapters involves the diffusion of CO_2 and H_2O molecules through porous soils and the stomatal pores of leaves. The presence of pores within an otherwise non-porous surface, creates complexities in the distribution of scalar concentration gradients. Imagine an impermeable surface punctuated with holes through which smoke diffuses into a still atmosphere. Immediately adjacent to the surface, the distribution of smoke would be highly variable; with areas of high smoke density above the holes and areas of low density in between the holes. As the smoke emanates from the holes it disburses as progressively expanding shells that eventually merge into a nearly homogeneous layer of smoke at some distance above the surface. Clearly, the concentration of smoke varies across the surface and given the dependence of diffusion rate on concentration gradients, the rate of diffusion will be concomitantly variable. Estimation of a mean diffusion rate for the surface will depend on the size and distribution of the holes. Furthermore, as smoke diffuses through the holes it's dispersion pattern will change as a function of distance. As it passes through the 'throat' of the hole it will diffuse in near-linear manner, perpendicular to the main axis through the pore. Once it exits the hole, it will disperse into hemispherical space above the hole. The diffusive resistance offered by the restricted cross-sectional area across which the smoke can move, and the volume of the hemispherical space into which can disperse upon leaving the hole, will be dependent on the dimensions of the hole. There are clearly reasons to suspect that diffusion through pores is a much different process than diffusion across open space. Here, we try to resolve some of the most important facets controlling diffusion across porous surfaces.

5.B.1 The paradox of pores

The diffusion of mass through a pore does not follow Fick's law in simple fashion. In fact, diffusion through a porous surface is much more efficient (higher diffusive flux per unit of open surface area) than diffusion from a non-porous surface. For example, the total diffusive fluxes of water vapor across a porous leaf surface and open pan of water are approximately equal, despite the fact that the pore area of the leaf surface is only 1-2% the total surface area of the pan of water. What is the explanation for the higher diffusive efficiency of porous surfaces?

In still air, molecules that diffuse across a pore disperse with equal probability into space above the pore. Thus, a shell of contours exists with concentration gradients extending outward from the pore (Figure 5.1). The steepest part of the gradients (i.e., the path with highest $\partial c/\partial x$) will occur along vectors fanning out from the perimeter of the pore at the lowest possible angle. In the case of a porous evaporating surface, where the ratio of perimeter circumference to total open surface area is greater than for an open pan of water, the potential for diffusion across the steepest part of the diffusion gradient is also greater.

The rate of diffusion from the open surface of a pore, large or small, scales differently with regard to the characteristic dimension of the surface, compared to diffusion along a linear distance. Considering Fick's law it is clear that linear distance, x, is a controlling variable with regard to diffusion rate (see Equation 5.1). When distance, x (in m), is combined with volumetric concentration, c (in mol m^{-3}), and diffusion coefficient, K_d (in m^2 s^{-1}), in Equation 5.1, the resultant flux rate is expressed per unit of cross-sectional area (m^2). In the case of diffusion from the open surface of a pore, however, flux rate scales with diameter of the pore, *not cross-sectional area*. The differences between diffusion from pores, as opposed to across linear distance, emerge directly from the 'perimeter effect'; the same effect that influences diffusion efficiency. To understand these relations, let's constrain diffusion across linear distance by imposing the condition that it occurs through a tube with solid walls. The walls will constrain the diffusive flux to the axis perpendicular to the length of the tube. The diffusive flux predicted by Equation 5.1 is expressed per unit cross-sectional area, so if we increase the cross-sectional area of the tube by a factor of 2, but leave the length of the tube unchanged, the diffusive flux per unit area will remain the same, but the total flux will increase by a factor of 2. This relation does not hold true for the case of diffusion from an open, circular surface. Using circular dishes of water with different surface diameters, the rate of evaporation per unit area decreases exponentially as the diameter of the dishes increases; the total evaporation rate will increase, but the evaporation efficiency decreases (Fig. 5.2). This is because the highest evaporation efficiency is occurring at the perimeter of the dishes. The cross-sectional area of dishes will increase as a function of $\pi(d/2)^2$, but the circumference will only increase as a function of πd, where d is the diameter of the dish. As cross-sectional area increases, the circumference will not increase proportionately, and the diffusive flux per unit of cross-sectional area will decrease. Stated another way, the presence of hemispherical shells of progressively decreasing scalar density outside the opening of pores imposes an influence on diffusion rate over and above that represented by the depth and area of the pores itself. The shape of the diffusion field has changed in a way that favors diffusion from the edges of the field and deters diffusion through the central axis running perpendicular from the pore surface. The relation between diffusive flux and pore diameter, rather than cross-sectional area was first formalized in 1881 when Josef Stefan, an Austrian physicist, came to the conclusion that diffusion from open pools of water in relatively still air is proportional to the diameter of the pools.

5.B.2 Diffusive resistance and conductance

Within the apparent simplicity of Fick's first law we can find powerful insight into the underlying physical processes that determine the diffusive flux. Diffusive fluxes can be scaled directly to a 'driving force' that reflects inequalities in statistical probability, and inversely to a 'mitigating resistance' that reflects inherent constraints working against the driving force. Here, we refer to the ***driving force*** as a force that induces motion in the diffusing entity; in the case of Fick's law, that force is traced back to the thermal motion of the diffusing particles and scales linearly with the concentration gradient. The mitigating ***resistance*** reflects forces that oppose the driving force. The mitigating diffusive resistance is due to friction that is induced when diffusing particles move trough a fluid; exchanging places in binary fashion with other particles. We can also think of the 'mitigating resistance' in terms of a 'facilitating conductance'; where ***conductance*** is defined as the inverse of resistance.

To elaborate further on the concept of resistance, a diffusive flux can be considered as an analogue to the electrical flux of electrons. An electrical current is propelled by an electrical potential difference between two points, which we can characterize as a driving force, and mitigated by an electrical resistance, in this case due to frictional forces that develop as the current is conducted through wire, or some other conductive medium. Electrical current and resistance can be mathematically related to the difference in electrical potential by ***Ohm's Law***: $I = \Delta V/r$; where I is the electrical current, ΔV is the voltage difference between two points, and r is the electrical resistance. Making a mathematical analogy between electric current and a diffusive flux, we can describe the difference in concentration between two points (Δc) as analogous to the difference in electrical potential (ΔV) and we can develop the concept of a diffusive resistance ($\Delta x/K_d$) as being analogous to the electrical resistance (r).

We can now appreciate the effect of pores as they impose a diffusive resistance that at the same time facilitates and impedes the movement of molecules across a surface. Imagine a non-porous surface, with infinite resistance to the passage of molecules that happen to collide with it; in essence, no molecules will pass and the diffusive flux is zero. If we now allow the sparse introduction of pores into the surface, the diffusive resistance will be relaxed to some extent; assuming that the pores are spaced far enough apart, the exact resistance will be determined solely by the density, size and shape of the pores. The resistance to diffusion will be due to the frictional interactions between molecules and the walls of the pore as they pass through, and the degree to which the pore influences the depth and steepness of the scalar concentration gradient that develops above the pore; i.e., the degree to which the presence of the pores induces the formation of hemispherical scalar concentration shells, and thus influences the diffusive driving force. As we allow the density of pores to increase, the hemispherical shells of scalar concentration that develop above one pore will begin to merge with those of neighboring pores closer to the surface. Thus, synergistic interactions among neighboring pores will begin to influence diffusive resistance of the surface as a whole. As the density of the pores increases even further, the overlapping shells will merge into a continuous boundary layer of decreasing scalar concentration in the coordinate perpendicular to the surface. From this example it is clear that diffusive resistance across a surface is due to the synergistic interaction of frictional forces within the pore and influences on the concentration gradient above the pore.

5.B.3 Pure diffusion versus advection

In its most fundamental context, flux is driven by gradients in chemical potential. Chemical potential is a thermodynamic concept that is influenced by pressure, temperature and concentration (see Section 2.B). As discussed above, however, diffusion is also defined in its purest terms as a process of binary molecular exchange. Binary exchange implies the movement of single, interacting molecules, as opposed to the bulk movement of a whole population of molecules propelled forward by movement in surrounding fluid. We refer to true binary exchange as *pure diffusion*, a process that responds most directly to gradients in concentration. Bulk movement due to motion in the entire fluid, which responds most directly to gradients in temperature and pressure is referred to as *advection*.

To put these concepts into a more concrete picture imagine a leaf with a stream of transported H_2O molecules exiting the leaf into the atmosphere. The relevant concentration gradient for H_2O exchange between the leaf and atmosphere is that occurring between the intercellular air spaces of the leaf and the well-mixed air above the leaf. We can express an averaged form of this concentration gradient across finite space, as $\Delta c_w/\Delta z$, where c_w refers to the concentration of water molecules and z refers to distance in the vertical coordinate across the leaf surface. The principal barrier separating the air in the intercellular air spaces and the atmosphere is the leaf epidermis, with its associated leaf (stomatal) pores. If the mean pressures and temperatures of the intercellular air spaces and atmosphere in the vicinity of the stomatal pores are equal, then H_2O will be transported through the pores solely in response to the concentration gradient; reflecting pure diffusion. Imagine, however, a situation in which the leaf absorbs solar energy, which increases the leaf's temperature to a value above air temperature. The pressure and temperature of the air in the intercellular air spaces will be higher than that of the atmosphere, and air will be forced through advective flow, out the leaf through the stomatal pores. In this case, the transport of H_2O molecules out of the leaf will be due to a combination of diffusion and advection. In fact, leaf transpiration reflects both of these processes in the real world; pressure and temperature equilibrium across leaf surfaces seldom exist under natural conditions.

Pure diffusive flow through a porous surface will occur, even in the presence of local pressure and temperature gradients if the pore size is small enough. Pores with diameters on the order of 1 μm or less approach the mean free path length of air molecules, including H_2O.[1] As the mean free path of air is approached, molecules are much more likely to contact the walls of the pores as they pass through, and advective flows are suppressed. In this condition, diffusion approaches a process of pure binary, molecular exchange. The diffusion coefficient for transport under these conditions will be significantly reduced. The ratio of the mean free path for a diffusing scalar and a representative length scale that controls the rate of diffusion is the ***Knudsen number*** (Kn); the Knudsen number is dimensionless and formally defined as:

$$Kn = \frac{\lambda_p}{L} \qquad (5.3)$$

where λ_p is the mean free path and L is the representative length scale (both with units of length). Thus, for the case of a scalar entity with relatively low density diffusing through a micropore with narrow diameter, Kn will be relatively large. Constituents diffusing in such systems are said to be diffusing according to ***Knudsen flow***. By convention, we assume that Knudsen flow occurs when Kn is approximately 1 or higher; although there are no definitive thresholds in this regard. Stomatal pores in leaves typically have diameters of 20-50 μm when fully open (although it should be noted that these pores are seldom circular in shape, but rather elliptical.) When closed, the residual opening of the stomatal pore is on the order of 1-2 μm. Thus, when leaves are transpiring H_2O at high rates, the pores exhibit diameters that are well beyond those that facilitate Knudsen flow.

In pure diffusive binary exchange, molecules will encounter a mitigating resistance that is proportional to their mass; heavier molecules will encounter more resistance. This relation was formalized in a mathematical relationship known as *Graham's Law*, originally described by the Scottish chemist, Thomas Graham, in 1881. Graham's Law is stated as:

$$\frac{F_1}{F_2} = \sqrt{\frac{m_2}{m_1}} \qquad (5.4)$$

where F_1 and F_2 are the diffusive fluxes of particles 1 and 2 with masses m_1 and m_2. In Knudsen flow, particles of different types will fractionate, due to differential diffusive fluxes related inversely to their masses. As flows through pores shift toward favoring advective, bulk flow the fractionation described by Graham's Law will weaken. Thus, the greatest fractionation on the basis of molecular mass will occur when flows are directed through pores with the smallest diameters. We will return to this phenomenon when we discuss stable isotope fractionation in photosynthesizing leaves.

5.C Flux divergence, continuity and mass balance

One of the more useful concepts that we can consider within the context of biogeochemical fluxes involves the linkage of flux divergence (changes in the magnitude of fluxes) across space to concentration divergence (changes in the magnitude of concentration) across time. In fact, this linkage of flux to concentration, which we have already established with regard to diffusion (see Equation 5.1), will be a recurrent theme in future chapters as we consider larger scales of space and time. In order to illustrate the coupling between flux and concentration, consider a well-mixed volume within which is contained a leaf (Fig. 5.3). If air is flowed into the chamber through a defined inlet at flow rate u_{in} (units of $m^3\ s^{-1}$) and it contains scalar entity at concentration c_{in} (units mol m^{-3}), and it flows out of the chamber at a defined outlet at rate u_{out} and concentration c_{out}, and assuming no accumulation of scalar in the chamber (i.e., assuming steady-state with regard to scalar concentration), we can determine the flux by which the scalar is removed from the air as the difference ($u_{in}c_{in} - u_{out}c_{out}$). This difference would equal the total sink strength of the leaf (S). This is the calculation and approach used to measure the net CO_2 exchange rate of leaves within gas-exchange chambers. In that case, S is expressed per unit of leaf area, or as $(u_{in}c_{in} - u_{out}c_{out})/L$, where L is leaf area (units m^2).

A similar approach can be used to determine the sink strength of an entire stand of vegetation. In this case, consider an imaginary, controlled volume which encloses a stand of vegetation and the air immediately above, and measurements of the flux of a scalar from a tower located immediately downwind from the volume (Figure 5.3). Thus, air is advected through the volume by the wind and then measured downwind as it reaches the tower. The ground area containing the vegetation 'sensed' by the tower is the flux footprint. We will designate the flux of a scalar that enters the upwind face of the volume as F, which is expressed as flux per unit of face area (e.g., mol m^{-2}). Furthermore, let's assume that: (1) a sink (S) exists within the volume such that some fraction of the scalar carried by F is assimilated per unit time, and (2) that the air in the volume is not well-mixed, meaning that variations in flow rate and scalar concentration can occur in the x-coordinate as the air flows across the footprint (we will ignore components of the flow along the y- and z-coordinates in the interest of simplicity). As in the case for a leaf chamber, the total flux at the exiting face will be less than that at the entering face by an amount equal to the cumulative effect of S, plus any scalar that accumulates in the chamber over time. Following these assumptions, we can write:

$$\mathrm{F}\,A_{\mathrm{r}} - \left[\mathrm{F} - \int_{x1}^{x2} \left(\frac{\partial \mathrm{F}}{\partial x}\right) dx\right] A_{\mathrm{r}} = A_{\mathrm{r}} \int_{x1}^{x2} \left(\frac{\partial \mathrm{c}}{\partial t}\right) dx + A_{\mathrm{r}} \int_{x1}^{x2} \mathrm{S}\, dx \qquad (5.5)$$

The spatial integral of the change in flux as a function of distance (x) on the left side of Equation 5.5 is known as the *flux divergence* (i.e., $\partial F/\partial x$). If the system is at steady state with regard to scalar concentration within the hypothetical volume (i.e., if $\partial c/\partial t = 0$), then the flux divergence must be equal to cumulative sink activity. Using Equation 5.5, we can calculate the mass balance for the volume given the presence of spatial and temporal divergences in the flux and concentration, respectively. (Equation 5.5 can just as easily be expressed to account for the presence of a scalar source, in which case the flux of scalar from the exiting face will be greater than that at the entering face.) Simplifying Equation 5.5, we obtain:

$$-\frac{\partial \mathrm{F}}{\partial x} = \mathrm{S} + \frac{\partial \mathrm{c}}{\partial t} \qquad (5.6)$$

Equation 5.6 is known as the *continuity equation*. In essence, the continuity equation states that any decrease in the flux of scalar across space within a controlled volume, must be balanced by the sink activity that assimilates that scalar across the same space plus any time-dependent accumulation of scalar within the volume. Thus, the volume must adhere to the constraint of *mass balance*. Once again, Equation 5.6 can be expressed with regard to a scalar source by changing the sign of S to be negative. We could also expand Equation 5.6 to account for spatial divergence in the *y*- and *z*-coordinates, and divergences in the turbulent and mean components of the flow, which we will in fact consider in a future chapter when we discuss eddy fluxes (see Chapter 9).

5.D Osmosis and water potential

Osmosis is a special case of diffusion in which a solvent, as opposed to a solute, diffuses across a selectively permeable membrane from a solution with low solute concentration to a solution with high solute concentration. A selectively permeable membrane permits certain, but not all solute or solvent molecules to cross. Selectivity is imposed by the nature of the membrane and the nature of any pores in the membrane. In biological systems, osmosis is most relevant to the flux of water across a phospholipid bilayer membrane. Cellular membranes are constructed from phospholipid bilayers. The phospholipid matrix of the membrane is hydrophobic, and is thus impermeable (though not ideally so) to most charged or electrically polar solutes. The membrane is also *dynamic*, meaning that the phospholipid molecules continuously move back and forth laterally along the length of the membrane. This lateral movement creates transient pores wherein water molecules, due to their small size, can potentially cross. The limited nature of the phospholipid movement, and transient nature of pores, imposes a diffusive resistance to osmotic diffusion. Alternatively, protein pores, known as *aquaporins*, are known to transverse the phospholipid bilayer, facilitating the diffusion of water molecules (Kaldenhoff et al. 2008). Aquaporins are also selective as to which molecules can pass, according to size and charge, such that charged ions and most solutes cannot pass. Water molecules cross the aquaporin channels in a single-file line, once again emphasizing that while aquaporins enable osmosis, they are constrained to do so with a finite diffusive resistance.

Osmosis occurs from one reservoir of solution to another, across a membrane that separates the two solutions. The solution that contains the higher solute concentration is defined as *hypertonic* relative to the solution with lower solute concentration. Conversely, the solution with lower solute concentration is defined as *hypotonic*. Osmosis can also be defined in thermodynamic terms. A free-energy gradient exists from the hypotonic solution, where collisions among water molecules are more frequent, compared to the hypertonic solution, where collisions among water molecules are less frequent. On this basis alone it is clear that water has more potential to do work in the hypotonic solution. However, the frequency of collisions is not only affected by the relative concentrations of water molecules, but also by the electrostatic attraction of polar water molecules for charged or polar solutes. Electrostatic attraction to solute surfaces reduces the free-energy of water molecules, and thus reduces their potential to participate in the collisions that drive osmosis. The chemical potential of the hypotonic solution, also known as the *water potential*, is higher compared to that of the hypertonic solution.

Water movement through plants requires that work be done to counteract the electrostatic forces that keep water molecules bound to soil particles, soil and plant solutes, the polar cellulosic surfaces of plant cell walls, and the gravitational forces that prevent water from rising above the surface. Water moves through biological systems according to free-energy gradients. Formally, water potential (ψ_w) is the thermodynamic capacity for a unit of water to do work. Water flows spontaneously from regions of higher ψ_w (higher free energy) to regions of lower ψ_w (lower free energy). By convention, the ψ_w of pure water at standard temperature and pressure is taken as zero. Also, by convention, ψ_w does not carry the typical units of free energy (J mol^{-1}), but rather units of pressure (Pa).[2] The chemical potential of water is influenced by four principal factors in biophysical systems; solutes, pressure, gravity and matrices. Three of the four factors – solutes, gravity and matrices – reduce the chemical potential of water relative to its pure state (or, in the case of gravity, relative to pure water at the earth's surface). In other words, they reduce the potential for water to do work.[3] Pressure can either increase or decrease the chemical potential of water depending on whether it is a positive or negative pressure, respectively.

The addition of solutes to water will reduce the capacity for the resulting solution to do work (i.e., reduce its free energy) by reducing the mobility of water molecules as they are attracted to the charged or polar surfaces of the solutes; thus, the addition of solutes results in an *osmotic potential* (ψ_π) which is negative in value (i.e., $\psi_\pi < \psi_w$). The osmotic potential can be represented as $\Psi_\pi = C\, R\, T$, where C is the concentration of solutes (mol m^{-3}), R is the gas constant (8.31 m^3 Pa mol^{-1} K^{-1}), and T is temperature (K).

The addition of a positive pressure to the solution will increase its free energy by increasing the mobility of water molecules. Negative pressures (tensions) often develop in transpiring plants as water moves from the soil (with higher ψ_w) to the atmosphere (with lower ψ_w). Tension in the xylem of plants reduces the capacity for the water to do work. The pressure potential (Ψ_p) is equal to the absolute pressure of the water system minus atmospheric pressure ($\Psi_p = P_w - P$).

As water moves up a tree it comes under the influence of gravitational forces that resist its ascent. The gravitational resistance reduces the free energy of water as it moves higher, producing a gravitational component to water potential (Ψ_g), which is negative in sign. The gravitational potential is defined as $\Psi_g = \rho_w\, g\, h$, where ρ_w is the density of the water (kg m^{-3}), g is gravitational acceleration (9.81 m s^{-2}), and h is height above the ground (m). The value of Ψ_g can be a significant in tall trees, such as the redwood trees that dominate some forests in the Western United States.

Matric potential (Ψ_m) refers to the effect of a large polar or charged surface (matrix) in the water system. In biophysics, this is most relevant in soil, where soil particles and organic matter surfaces can interact with water molecules. The matric effect reduces the free energy of water molecules through attractive forces that reduce their mobility; thus, it is negative in sign. It is not possible to derive one theoretical relationship to define Ψ_m, but rather it is dependent on the specific characteristics of the matrix causing the effect.

The total water potential of a system is reflected in the sum of its component potentials: $\Psi_w = \Psi_\pi + \Psi_p + \Psi_g + \Psi_m$. Gradients in Ψ_w provide the framework for understanding water fluxes. Evaporation occurs because of the large difference in the Ψ_w of the atmosphere compared to that in the soil. Water is driven from the soil, through plants and into the atmosphere according to progressively more negative water potentials along the so-called soil-vegetation-atmosphere continuum (Fig. 5.4). In living plant cells, water fluxes between the solution outside the cell (the apoplast) and inside the cell (the symplast) underlie several important ecophysiological processes, such as stomatal opening and closing, which exert a major control over surface-atmosphere gas exchange.

5.E Surface energy budgets

The solar radiation that strikes a surface will be reflected, absorbed or transmitted. Given this fundamental constraint, the solar radiation component of the energy budget for a surface can be expressed as:

$$R_s\, a = R_s\,(1 - r - t) \qquad (5.9)$$

where R_s is the short-wave incident flux (often expressed in radiant energy units of W m^{-2}), and a, r and t are the fractions of R_s that are absorbed, reflected and transmitted, respectively. Using these relations, and our knowledge about the emission of long-wave radiation (see Section 2.F), we can describe the *net radiation balance* (R_n, in units of W m^{-2}) for a surface as:

$$R_n = R_s\, a_s + R_L\, a_L - \varepsilon\sigma T_s^4 \qquad (5.10)$$

where R_s is the incident shortwave radiant energy (W m^{-2}), a_s is the fractional absorptance of the surface with respect to R_s, R_L is the long-wave radiant energy (W m^{-2}) absorbed from the sky and surrounding objects, a_L is the fractional absorptance of the surface for long-wave radiation, and the Stefan-Boltzmann expression represents the loss of long-wave radiant energy from the surface with temperature equal to T_s (K).

The net radiation energy absorbed by a surface must be dissipated or channeled into the kinetic energy of the surface mass, which in turn will increase the temperature of the surface. After accounting for re-radiation of long-wave radiant energy, the principal processes leading to energy dissipation by a surface are latent and sensible heat loss. *Latent heat* (units of W m^{-2}) is lost when energy absorbed by the surface is converted into the kinetic energy of water molecules which are subsequently transported from the surface, carrying their kinetic energy with them. Latent heat can also be gained when water molecules leave the vapor phase of the atmosphere and condense on a surface (e.g., as dew), releasing heat. The amount of latent heat that is lost from, or gained by, a surface depends on the *latent heat of vaporization* (λ_w), a coefficient that is sensitive to temperature (ranging from 2.48 MJ kg^{-1} at 10°C to 2.41 MJ kg^{-1} at 40°C). Thus, the rate of evaporative latent heat exchange is calculated as $\lambda_w E$, where E is rate of evaporation in units of moles or mass of H_2O per unit surface area per unit time.

Sensible heat is exchanged through conduction between a surface and air molecules that contact the surface. Sensible heat gets its name from the fact that, unlike latent heat, sensible heat can be sensed directly as the heat moves from one point to another. The rate of sensible heat exchange (H_{se}) between the surface and atmosphere is determined by the thermal conductivity of air and the thermal gradient between the surface and air:

$$H_{se} = -K_h \frac{dT}{dz} \qquad (5.11)$$

where H_{se} is the sensible heat flux and carries units of J m^{-2} s^{-1}, T is temperature in units of K, z is distance in units of m, and K_h is the diffusion coefficient for heat in units of J m^{-1} s^{-1} K^{-1}. In this case, dz is the distance that spans the contact point of an air molecule that collides with the surface. The form of Equation 5.11 should invoke recognition of similarities with Equation 5.1, which describes the diffusion of mass according to Fick's first law. The rates of sensible and latent heat exchange are to a large degree mutually coupled. Energy that is absorbed by a surface, but not lost through the latent heat path, will contribute to a rise in surface temperature, causing an increase in sensible heat flux. Thus, in surface energy budgets we often refer to the *coupled partitioning* of absorbed energy between latent and sensible heat. This partitioning will depend on many factors associated with both the surface and atmosphere, including surface wetness, transport resistances from the surface to the atmosphere and atmospheric humidity.

5.E.1 Latent heat, atmospheric humidity and temperature

Latent heat exchange is an important flux between plants and the atmosphere because it combines components of both mass and energy fluxes. The surface-atmosphere flux of latent heat is dependent on atmospheric humidity, which is in turn dependent on air temperature. Additionally, with regard to leaves, latent heat loss to the atmosphere is dependent on the difference in humidity between the air inside the leaf and that outside the leaf; once again, this difference is influenced by both leaf temperature and air temperature. Thus, it's worth spending some time discussing the complex relations between latent heat exchange, atmospheric humidity and temperature.

The fact that water vapor diffuses from a region of higher concentration to a region of lower concentration can be justified in thermodynamic terms according to differences chemical potential between the two regions. Imagine a parcel of air resting on a wet surface, and containing as much water vapor as it can possibly contain; i.e. saturated with water vapor. Imagine further that above that parcel of air rests another drier parcel with a less-than-saturated amount of water vapor. Water vapor will diffuse from the lower parcel to the higher parcel because the chemical potential of water vapor in the lower parcel is higher. To clarify the relation between atmospheric water vapor concentration and its thermodynamic chemical potential, we define the chemical potential of water (μ_w) as:

$$\mu_w = \mu_w{}^* + R\,\mathrm{T}\ln\frac{c_{wa}}{c_{wa}{}^*} \qquad (5.12)$$

where c_{wa} is the unsaturated concentration of water vapor in air and c_{wa}* is the saturated water vapor concentration in air at the same temperature (assuming no significant gravitational potential associated with height, standard pressure, and recognizing that water is an uncharged chemical species). Thus, as c_{wa} increases, and moves closer to c_{wa}*, the chemical potential of water vapor in the atmosphere increases.

The saturated water vapor concentration of air (c_{wa}*) is itself a function of temperature. This relation is often expressed as a derived form of the Clausius-Clapeyron relation:

$$\frac{d\,c_{wa}{}^*}{d\mathrm{T}} = \frac{\lambda_w}{\mathrm{T\,P}\,\Delta V} \qquad (5.13)$$

where ΔV is the difference in specific volume between the liquid and vapor states, and in this case stating the relation in terms of water vapor mole fraction, rather than water vapor partial pressure (e_s), as is often done. A derivation of the Clausius-Clapeyron relation from thermodynamic principles is presented in Appendix 5.2. One of the fundamental relations to emerge from derivation of the Clausius-Clapeyron equation is:

$$\frac{d\mathrm{c_{wa}}^*}{\mathrm{c_{wa}}^*} \approx \frac{\lambda_w}{\mathrm{n}R}\frac{d\mathrm{T}}{\mathrm{T}^2} \qquad (5.14)$$

from which we can define the slope (ε) of the increase in c_{wa}* as a function of temperature as:

$$s = \frac{d\mathrm{c_{wa}}^*}{d\mathrm{T}} \approx \frac{\lambda_w}{\mathrm{n}R}\frac{\mathrm{c_{wa}}^*}{\mathrm{T}^2} \qquad (5.15)$$

In other treatments in the meteorological literature, *s* is sometimes referred to as Δ. The value of *s* is useful for understanding the response of atmospheric humidity and changes in the chemical potential of water as atmospheric temperature increases. We will return to consideration of *s* when we derive the Penman-Monteith model for surface-atmosphere evapotranspiration in the next chapter.

The Clausius-Clapeyron relation is difficult to use for routine work relating atmospheric saturation water vapor concentration to temperature, so a more useful relation is often used:

$$\mathrm{c_{wa}}^* = \frac{a}{\mathrm{P}}\exp\left(\frac{b\mathrm{T}}{\mathrm{T}+c}\right) \qquad (5.16)$$

where T is expressed in units °C and P is in Pa, and *a*, *b* and *c* are empirical constants with general values being *a* = 0.611 kPa, *b* = 17.502 and *c* = 240.97 °C (see Buck 1981). A plot of the relation between c_{wa}* and T using Equation 5.16 is shown in Figure 5.5, demonstrating the exponential nature of the function.

Atmospheric humidity is expressed in a variety of ways, many of which have emerged from the meteorological research community. Some of the most common forms of expression are dew point, relative humidity, saturation vapor deficit, and wet-bulb temperature. The *dew point* (T_d) of a volume of air is the temperature to which the air must be cooled, without a change in pressure or water vapor density, in order for its vapor density to reach the saturation point; i.e., the temperature at which $c_{wa} = c_{wa}$*. The dew point is the temperature of a sample of air at which the relative humidity is 1.0 (or 100%). *Relative humidity* (h_r) is defined as the ratio of actual water vapor concentration to the saturation water vapor concentration at the same temperature; i.e. $h_r = c_{wa}/c_{wa}*$. The *atmospheric saturation vapor deficit* is often used in micrometeorological studies of latent heat flux and refers to the difference between the saturation water vapor concentration and the actual water vapor concentration; i.e., $c_{wa}* - c_{wa}$.

We need to spend a bit more time discussing the concept of wet-bulb temperature (T_w), as we will use it in future sections as a core concept in surface energy budgets. The *wet-bulb temperature* is the temperature a sample of air would have if it were cooled by evaporation alone, adiabatically to the point where $c_{wa} = c_{wa}*$. In other words, it is the lowest temperature a sample of air can achieve if cooled only by evaporation; noting that evaporation will cease when $c_{wa} = c_{wa}*$. The wet-bulb temperature is often defined relative to the *dry-bulb temperature*, which in turn reflects the temperature of a dry sensor not subjected evaporative cooling. To illustrate the concept of wet-bulb and dry-bulb temperatures, consider a sample of air with unsaturated water vapor density, open to a source of liquid water, but insulated from energy exchange with its surroundings (i.e., a sample with adiabatic energy balance). Because the air is unsaturated (i.e., with a positive atmospheric saturation vapor deficit), water will evaporate from the water surface, adding latent heat to the air. Given the stipulation that evaporation occurs adiabatically, the energy to evaporate the liquid water must come at the expense of sensible heat within the sample of air. That is, sensible heat must be transferred from the air to the water surface, where it is used to evaporate water into the air. We can verify these exchanges by measuring a decrease in 'sensed' temperature of the air; it will cool. The vapor pressure of the air will increase, along with its increase in latent heat, and the chemical potential of water in the air will also increase. Eventually, the system will come to equilibrium when the chemical potential of water in the air equals that of the liquid water, and the ratio $c_{wa}/c_{wa}* = 1.0$. At that point, the system will have cooled to the wet-bulb temperature. With knowledge of the dry and wet-bulb temperatures we can estimate the original, unsaturated, water vapor mole fraction of the air (c_{wa}) as:

$$c_{wa} = c_{wa}^* - \gamma\left(T_a - T_w\right) \qquad (5.17)$$

where $c_{wa}*$ is the saturation water vapor mole fraction at the wet-bulb temperature, γ is the *psychrometer constant*, defined formally as c_p/λ_w, where c_p is the is the specific heat of air (J mol^{-1} K^{-1}), T_a is the dry-bulb temperature and T_w is the wet-bulb temperature. Thus, one really only need know the wet and dry bulb temperatures and γ to characterize the thermodynamic state of moist air. The term 'constant' is a bit of a misnomer for describing γ, as γ will vary slightly with temperature due to the temperature dependence of λ_w. Note that the units of γ are change in mole fraction per K; the same units as those used for *s* (see Equation 5.15). In fact, both γ and *s* can be used to convert a difference between dry and wet-bulb temperatures into a mole fraction water vapor concentration (the unsaturated water vapor concentration in the case of γ and the saturated water vapor concentration in the case of *s*). Thus, somewhat analogous to our definition of γ in Equation 5.17, we can define *s* within the context of dry- and wet bulb temperatures, according to:

$$c_{wa}{}^{*}{}_{(T_w)} \approx c_{wa}{}^{*}{}_{(T_a)} - s\left(T_a - T_w\right) \qquad (5.18)$$

where $c_{wa}{}^{*}{}_{(Tw)}$ refers to the saturated water vapor mole fraction at the wet-bulb temperature and $c_{wa}{}^{*}{}_{(Ta)}$ refers to the saturated water vapor mole fraction at the dry-bulb temperature. The approximation sign in Equation 5.18 is required because of a simplifying convenience that is introduced to permit the assumption of linearity in the relation between c_{wa}* and T_a (discussed in the next section). We can relate *s* and γ to each other according to:

$$c_{wa}{}^{*} - c_{wa} \approx \left(s + \gamma\right)\left(T_a - T_w\right) \qquad (5.19)$$

where $c_{wa}{}^{*}$ and c_{wa} represent the saturated and unsaturated water vapor mole fractions at the dry-bulb temperature, respectively. The relation defined in Equation 5.19 will be come important when we discuss the coupling of leaf and soil energy budgets to evapotranspiration rates. The difference in water vapor concentration across a surface (i.e., $c_{wa}{}^{*} - c_{wa}$) is related to the difference in surface-to-air temperature according to the constraints described in Equation 5.19.

In practice, the wet-bulb temperature of the atmosphere can be measured by covering the bulb of a mercury-in-glass thermometer with a wet cotton sleeve which is well-ventilated and allowed to reach evaporative equilibrium with the surrounding air; the temperature that is reached at that equilibrium point is the wet-bulb temperature. The dry-bulb temperature can be measured with a 'dry' temperature sensor, such as dry mercury-in-glass thermometer, located next to the 'wet' sensor. Instruments designed to measure the wet- and dry-bulb temperatures are called _psychrometers._

5.E.2 Surface evaporation

"Two requirements must be met to permit continued evaporation. There must be a supply of energy to provide the latent heat of vaporization, and there must be some mechanism for removing the vapour, i.e., there must be a sink for the vapour. Analytical attacks on the problem start from one of these two points…"

H.L. Penman (1948)

Different and (sometimes) opposing perspectives have been used historically to derive the causes and constraints on evaporation (Jarvis and McNaughton 1986). Meteorologists often approach evaporation from the thermodynamic perspective, focusing on the *energy* that is required to drive the latent heat of vaporization (or condensation). Biologists will also take this perspective within the context of leaf or canopy energy budgets, but more often they are concerned with the loss of H_2O mass from a plant, rather than latent heat. Thus, they focus on issues such as the ratio of H_2O/CO_2 exchange, or the rate of plant transpiration and its influence on plant water balance. Using this latter perspective, focus shifts from energy balance to the *potential difference* between the humidity of the surface and the free atmosphere. As described so pointedly in the quote above from Howard Penman, both perspectives are required for a full understanding of evaporation –energy must be absorbed by liquid water molecules in order to drive vaporization and a deficit of water molecules must exist in the atmosphere, providing a sink to accommodate the transport.

On a theoretical basis, these two requirements have been combined first in the so-called _Penman equation_, or _combination equation_, and later in the more-commonly used _Penman-Monteith equation_. In order to understand these combination models, we need to travel back to the middle of the past century to initial efforts by Charles Warren Thornwaite to estimate potential evaporation. _Potential evaporation_ is defined in hydrologic terms as: 'the evaporation from an extended surface of a short grass that is supplied with water and the canopy covers the ground completely.' Potential evaporation is used as a benchmark against which we can evaluate *actual evaporation*. Thornthwaite (Thornthwaite 1948) developed a relation that evaluated monthly potential evaporation (E) as a function of temperature (cm per month) and day length:

$$E = 1.6 \frac{L}{12} \frac{N}{30} \left(10 \frac{T}{I} \right)^{a} \qquad (5.20)$$

where L is daylength (h), N is number of days in a month, T is mean monthly air temperature, I is a heat index, computed as a function of the sum of 12 monthly temperature indices, and the exponent, *a,* is an empirical function of I. Thornwaite's method had several shortcomings: evaporation and temperature are out of phase with one another, there is no feedback to plants, and it could not be applied to short term studies, as temperature is not a suitable proxy for radiation at such time scales. Nevertheless, the method has found some favor by biogeographers (e.g., Rosenzweig 1968) who have used it to define general correlations between plant distributions and precipitation.

In the late 1940's, Penman (Penman 1948) recognized the weakness of the Thornthwaite approach. He consequently developed a relation that had a physical basis. In 1948, he derived the Penman equation:

$$\lambda_w E = \underbrace{\frac{s}{s+\gamma}(R_n - H_G)}_{\text{Term I}} + \underbrace{\frac{\gamma}{s+\gamma}\lambda_w E_a}_{\text{Term II}} \qquad (5.21)$$

where λ_w is the latent heat of vaporization for water (J mol^{-1} H_2O), E is the evaporation rate (mol H_2O m^{-2} s^{-1}), *s* is the slope of the relationship between saturation water vapor mole fraction and air temperature (mol H_2O mol^{-1} air K^{-1}), γ is the psychrometer constant (mol H_2O mol^{-1} air K^{-1}) ($\gamma = c_p/\lambda_w$ where c_p is the specific heat of dry air in units of J mol^{-1} air K^{-1}), R_n is net radiation (J m^{-2} s^{-1}), H_G is the heat flux conducted from the soil surface to deeper layers in the soil (i.e., not available for surface evaporation) (J m^{-2} s^{-1}), and E_a is the aerodynamic evaporative flux. E_a can be described according to a diffusive analog model scaled to the difference in water vapor concentration between air next to the surface and that in the well-mixed atmosphere above the surface:

$$E_a = \rho_a \left(c_{wa}* - c_{wa}\right) f(U) \qquad (5.22)$$

where ρ_a is the molar density of dry air (mol air m^{-3}), c_{wa}* is the saturation mole fraction of water vapor in air at the surface (mol H_2O mol^{-1} air), c_{wa} is the mole fraction of water vapor in the atmosphere above the surface, and U is wind speed (m s^{-1}). Thus, Penman's equation included an energy balance term (Term I) and a term describing the diffusive potential of surface-atmosphere exchange (Term II). The recognition that it is the combination of forcings – energy and diffusive – that drives evaporation, and representation in concise quantitative form, was a major intellectual breakthrough and greatly promoted our understanding of surface-atmosphere water exchange.

Penman's equation gained early popularity as it relied on simple meteorological variables. Using it, meteorologists were able to produce an accurate estimate of evaporation across England. A major and revolutionary breakthrough on quantifying evaporation was made by John L. Monteith, a colleague with Penman at the Rothamsted Research station in England. Monteith modified the Penman equation by introducing a canopy resistance. This is the basis of the Penman-Monteith equation (Monteith 1981). The primary benefit of including canopy resistance was that it connected the theory to a dynamic, vegetated surface; it provided the opportunity to expand the theory to include vegetative function. In order to appreciate a general derivation of the Penman-Monteith equation, we begin by stating that the evaporative rate of latent heat loss from a surface can be defined in diffusive terms as:

$$\lambda_w E = \frac{\rho_a c_p}{\gamma} \frac{\left(c_w * (T_s) - c_w\right)}{r_w} \qquad (5.23)$$

where r_w is the diffusive resistance to water vapor exchange (taken here as the aerodynamic resistance that forms when air is forced across a stationary surface). In energy budget terms we can write:

$$\lambda_w E = \frac{s}{s+\gamma}\left(R_n - H_G\right) \qquad (5.24)$$

Equation 5.23 reflects an Ohm's law diffusive analog model, whereas Equation 5.24 is derived from fundamentals of the surface energy balance; building from the assumption that the net radiation received by the surface is dissipated through latent heat exchange minus downward heat conduction. In order to combine Equations 5.23 and 5.24, we need to reconcile the fact that they are connected by a rather complex temperature feedback. Evaporation from a surface decreases the temperature of the surface, which in turn influences c_w^* (T_s). We can eliminate surface temperature from the equations through a mathematical convenience known as the Taylor Polynomial Theorem (see the Mathematical Concepts Appendix at the end of the book). If we assume that over a narrow range of temperatures (e.g., between T_a and T_s) we can estimate the slope of the relation between c_{wa}^* and T_a (which we represent as *s*) as being linear, and we can write (also see Equation 5.18):

$$c_{wa^*(Ts)} \approx c_{wa^*(Ta)} - s\left(T_a - T_s\right) \qquad (5.25)$$

Now, we follow several steps to: (1) use Equation 5.25 as a means to substitute for T_s and $c_{wa\,(Ts)}^{*}$, (2) recognize the relation between r_w and r_h (where r_h is the diffusive-analog, aerodynamic resistance to sensible heat transfer) as $\gamma^* = \gamma\ (r_w/r_h)$, and (3) conduct algebraic re-arrangement. In the final outcome, we derive the Penman-Monteith equation as:

$$\lambda_w E = \frac{s}{s+\gamma^*}\left(R_n - H_G\right) + \frac{\rho_a\, c_p\left(c_{wa^*(Ta)} - c_{wa(Ta)}\right)}{\left(s+\gamma^*\right) r_h} \qquad (5.26).$$

A formal derivation of the Penman-Monteith equation from a thermodynamic foundation, and derivation of its isothermal form, are provided in Appendices 5.3 and 5.4.

The Penman-Monteith equation is arguably the most widely-used model describing surface latent heat exchange in the field of micrometeorology. It has become popular in recent years among ecologists and plant physiologists as a means to predict surface resistances to water and heat transfer from canopies. When applied to individual leaves, the Penman-Monteith model can be used to partition stomatal and leaf boundary layer controls over water and heat exchange. We will return to the Penman-Monteith model in future chapters as we consider water exchange at these various scales.

Appendix 5.1 Derivation of Fick's First Law of Diffusion

We begin the derivation by recognizing that diffusion is a thermodynamic process driven by a gradient in chemical potential (μ). Chemical potential carries the same units as free energy per mole (joules mol^{-1}), and is therefore defined as the partial molar free energy for a chemical constituent. Thus, we can write:

$$f_D = -\frac{d\mu}{dx} \qquad (5.27)$$

where f_D is used to designate the molar 'diffusive force' and carries units of kg m s^{-2} mol^{-1} (or Newtons mol^{-1}), and recognizing that a joule of energy is equivalent to 1 kg m^2 s^{-2}. The negative sign on the right side forces the direction of the flux to occur opposite the direction of the gradient. The sign of the gradient is defined as positive when it increases from lower to higher concentration. Chemical potential can be defined in terms of the concentration of a constituent as:

$$\mu = \mu^* + R\mathrm{T}\ \ln \mathrm{c} \qquad (5.28)$$

where μ^* is the standard molar chemical potential (see Section 2.B), c is the mole fraction concentration. We assume that pressure is constant throughout the system. Differentiating Equation 5.27 with regard to distance (x) provides:

$$\frac{d\mu}{dx} = -R\mathrm{T}\frac{d\mathrm{c}}{dx} \qquad (5.29)$$

Equation 5.29 links the gradient in chemical potential to the gradient in concentration.

As a driving 'force', $d\mathrm{c}/dx$ is countered by a resistive 'force', which in large part represents the frictional interaction between molecules of the diffusing scalar as they move through the surrounding fluid (air or water). Friction is a 'force' with thermodynamic connotation. In dilute mixtures, friction involves collision between constituent molecules moving in the direction of the flux and molecules of the surrounding fluid. Molecular collisions redistribute mechanical energy to flux vectors other than that associated with the flux. In essence, collisions produce disorder from order. We can frame our discussion of diffusion within the context of 'mobility', whereby *diffusive mobility* refers to the capacity for a unit of molecules to move in the face of the resistive frictional forces they encounter in the fluid. We will define mobility (u) in mathematical terms according to the Einstein–Smoluchowski relation (Einstein 1905, Smoluchowski 1906):

$$u = \frac{\mathrm{v}}{f_D} \qquad (5.30)$$

where v is velocity (m s^{-1}) and u carries units of s mol kg^{-1}. After rearranging we can state:

$$f_D = \frac{\mathrm{v}}{u} = -R\mathrm{T}\frac{d\mathrm{c}}{dx} \qquad (5.31)$$

$$\mathrm{v} = -u\,R\mathrm{T}\frac{d\mathrm{c}}{dx} \qquad (5.32)$$

Relying further on Einstein's analysis (Einstein 1905), we can equate (u RT) with the diffusion coefficient originally derived by Fick (K_d), with units m^2 s^{-1}. Thus, the nature of K_d as a mobility term is clearly defined. To this point, we have derived the relationships in terms of molar units in order to make connections to the concepts of chemical thermodynamics. In order to place the derivation into a spatial framework, we can multiply both sides of Equation 5.32 by molar density (i.e., mol m^{-3}), producing the form of Fick's Law that we usually use with regard to *flux density*:

$$\mathrm{F} = -K_d\frac{d\mathrm{c}}{dx} \qquad (5.33)$$

where F is in units mol m^{-2} s^{-1}, K_d is units m^2 s^{-1}, and c is in units mol m^{-3}. In the case of the diffusion of a gaseous constituent (e.g., CO_2) through air, the partial pressure gradient (dp/dx), rather than the concentration gradient, is the relevant metric.

Appendix 5.2. Derivation of the Clausius-Clapeyron relation

The Clausius-Clapeyron relation is derived from initial assumptions regarding a thermodynamic system consisting of two phases (e.g., liquid and vapor), which we further assume to be at equilibrium. Assuming that the internal energy of the system does not change between the two phases ($\Delta U = 0$), we can write (see Section 2.A):

$$dG = V\,dP - S\,dT \qquad (5.34)$$

where G is Gibbs free energy, V is specific volume, P is pressure, S is entropy and T is temperature. Given that the two phases are at equilibrium, we know that $dG = 0$, such that we can write:

$$(V_1 - V_2)\,dP - (S_1 - S_2)\,dT = 0 \qquad (5.35)$$

where V_1 and S_1 are the respective specific volume and entropy for phase 1 and V_2 and S_2 are for phase 2. Rearranging, we obtain:

$$\frac{dP}{dT} = \frac{(S_1 - S_2)}{(V_1 - V_2)} \qquad (5.36)$$

We can define the latent heat of vaporization (for this particular case) as the amount of heat required to account for the change in entropy as water changes from liquid to vapor state in a reversible process, or in terms of the First Law of Thermodynamics as $\delta Q = T\,dS$ (see section 2.A). Thus $\lambda_w = T\,(S_1 - S_2)$, and we can write:

$$\frac{dP}{dT} = \frac{\lambda_w}{T\,(V_1 - V_2)} \qquad (5.37)$$

Equation 5.37 is the form of the Clausius-Clapeyron relation that is commonly used for studies of water evaporation in which P is equated to water vapor partial pressure (P_w). In order to express Equation 5.37 in terms of water vapor mole fraction (c_w), we use the relation $c_w = P_w/P$, where P_w is water vapor partial pressure.

We can use Equation 5.37 as the basis for deriving a general relation between the saturation water vapor concentration and temperature. We begin by assuming that the specific volume of water vapor in the gas phase (V_{wv}) is so much larger than the specific volume of water in the liquid phase that:

$$\frac{dP}{dT} \approx \frac{\lambda_w}{T\,V_{wv}} \tag{5.38}$$

Defining Equation 5.38 as pertaining to water vapor pressure (P_w), recognizing that PV = nRT (or $V_{wv} = nRT/P_w^*$, with P_w^* as the saturated water vapor partial pressure), and using $c_w^* = P_w^*/P$, we can write:

$$\frac{dc_w^*}{c_w^*} \approx \frac{\lambda_w}{nR}\frac{dT}{T^2} \tag{5.39}$$

Recalling rules of differentiation whereby $d\,x/x = d\ln x$, and logarithm rules whereby ln a – ln b = ln (a/b), we can write:

$$d\ln c_w^* = \frac{\lambda_w}{nR}\,d\left(-\frac{1}{T}\right) \tag{5.40}$$

Resolving the differential form of Equation 5.40, we can write:

$$c_{wa}^* = C\exp\left(-\frac{\lambda_w}{nRT}\right) \tag{5.41}$$

where C is a constant. Equation 5.41 shows the fundamental exponential relation between saturation water vapor concentration and air temperature that emerges from the Clausius-

Clapeyron relation. In practice, an empirical relation is used, the so-called Tetens formula (Buck 1981), which resembles the Clausius-Clapeyron relation:

$$c_w^* = \frac{a}{P}\exp\left(\frac{bT}{T+c}\right) \qquad (5.42)$$

where T is expressed in units °C and P is in Pa, and a, b and c are empirical constants with general values being a = 0.611 kPa, b = 17.502 and c = 240.97 °C.

Appendix 5.3. A thermodynamic approach to derivation of the Penman-Monteith equation

Penman's original mathematical treatment describing evaporation from a wet surface was developed from the premise that both surface energy balance and aerodynamic transport can be used to quantify the evaporative flux density. This conceptual framework was retained during later derivation of the Penman-Monteith equation. Here, we derive the Penman-Monteith equation from the first principles of thermodynamics. This approach is justified by the fact that evaporation can be defined as a flux that occurs due to disequilibrium within an open thermodynamic system.

We begin by defining our system as a wet surface coupled to an overlying volume of air with imaginary boundaries that distinguish it from the surrounding atmosphere. We apply the condition that the system is in a state of perennial disequilibrium, due to both a sustained moisture gradient (from surface to atmosphere) and a sustained flux of energy to the surface. The air above the surface can be defined according to a set of state variables including pressure, volume, mass, temperature and latent heat. In relating these state variables to one another, we can draw a graph showing saturation water vapor mole fraction (c_{wa}^*) as a function of temperature (Fig. 5.6), and we can define the molar sensible heat content and molar latent heat content of the air as $c_p T_a$ and $\lambda_w c_{wa}$, respectively.

Let's designate the initial state of our hypothetical air volume as point A on the graph in Figure 5.6. At this designation we know that the air exists with an unsaturated amount of humidity. The adiabatic, thermodynamic disequilibrium that exists because the air volume is in the unsaturated state can be defined by line AB. Line AB intersects the saturation curve at an angle (rather than parallel to the y-axis) because in the adiabatic state, the energy to increase the latent heat content of the air would have to come at the expense of the sensible heat content of the air. This means that the air must cool as sensible heat is transferred to the surface, driving evaporation and increasing atmospheric humidity. Thus, we can state: $\lambda_w E = - H_{se}$, and therefore the *total amount* of sensible heat that would need to be expended to evaporate water and move the air from point A to point B is $c_p (T_a - T_w)$, where c_p is the specific heat of air and T_w is the wet-bulb temperature. The *flux* of sensible heat (H_{se}), however, will be dependent on the difference between air temperature and surface temperature, $T_a - T_s$, not air temperature and the wet-bulb temperature, $T_a - T_w$. Thus, from a flux perspective we can define the sensible heat required to evaporate water and move the air from point A to point B as:

$$H_{se} = \frac{\rho_a c_p (T_a - T_s)}{r_h} = -\lambda_w E \tag{5.43}$$

where r_h is the transport resistance to sensible heat transfer between the surface and air with units s m^{-1}. The flux for H_{se} described in Equation 5.43 is constrained by the limit imposed when $T_a = T_w = T_s$. Now, we can call upon Equation 5.17 which states: $c_{wa} = c_{wa}* - \gamma (T_a - T_w)$, to define the latent heat transfer required to move air from point A to point B. In evaluating the latent heat flux from the surface to the atmosphere, once again, the relevant temperature is referenced to the surface (as in T_s), not to the air (as in T_w). Thus, we can write:

$$\lambda_w E = \frac{\rho_a c_p \left(c_{wa^*(Ts)} - c_{wa(Ta)}\right)}{\gamma\, r_w} \tag{5.44}$$

where r_w is the aerodynamic resistance for water vapor moving between the surface and the atmosphere. Recalling that $\gamma = c_p/\lambda_w$ (see section 5.E.1), we can relate r_w to r_h according to: $\gamma^* = \gamma\, (r_w/r_h)$. Combining Equations 5.43 and 5.44 we obtain:

$$-\frac{\rho_a c_p \left(c_{wa^*(Ts)} - c_{wa(Ta)}\right)}{\gamma\, r_w} = \frac{\rho_a c_p (T_a - T_s)}{r_h} \tag{5.45}$$

At this point, our analysis has been complicated by the fact that we have introduced two reference potentials for temperature in the equations – the surface and the air. Complications arise because both sensible heat transfer to the surface and latent heat transfer from the surface cause T_s to change. It would simplify matters if we could eliminate T_s and express the equations solely in terms of T_a. If we rely on the mathematical convenience provided by the Taylor Expansion Theorem to make the assumption that over the narrow range of temperatures between T_a and T_s we can estimate the slope of the relation between c_{wa}* and T_a (which we represent as s) as being linear, we can write:

$$c_{wa^*(Ts)} \approx c_{wa^*(Ta)} - s(T_a - T_s) \tag{5.46}$$

where $c_{wa}*_{(Ts)}$ is the saturated water vapor mole fraction at surface temperature. Now, we can use Equation 5.46 to define T_s, in terms of T_a. Following substitution of terms and algebraic re-arrangement we can write:

$$\lambda_w E = \frac{\rho_a c_p \left(c_{wa}{}^*{}_{(Ta)} - c_{wa(Ta)}\right)}{\left(s + \gamma^*\right) r_h} \tag{5.47}$$

Equation 5.47 represents the *adiabatic component* of the coupling between latent heat exchange and surface energy budgets. Once again, the adiabatic latent heat flux is limited to the point where $T_a = T_w$. If we now back off the adiabatic assumption, and allow the system to exchange energy with the surroundings, it's possible for the air to achieve temperatures higher than in the original unsaturated state, and for the water vapor saturation potential to increase accordingly. In this case, the fluxes of energy from the surroundings and associated latent heat flux would be defined as *diabatic processes*. The diabatic potential can be visualized in Figure 5.6 in which air moves from the state description at point A to the state description at point C. We can describe the transition from point A to point C as the sum of adiabatic and diabatic transitions described by lines AB and BC.

Diabatic energy absorption will cause an increase in air temperature, represented here as ΔT, and assuming that the air remains saturated with water vapor as the temperature increases, the change in water vapor mole fraction can be represented as $\Delta c_{wa}*$. Calling once again on Equation 5.17, we can write: $\Delta c_{wa}^* = s\,\Delta T$. Using this relation in Equation 5.38, we can write:

$$\lambda_w E = \frac{\rho_a c_p \left(s\,\Delta T\right)}{\gamma^* r_h} \tag{5.48}$$

where Equation 5.48 defines the latent heat flux associated with the diabatic increase in energy.

Now, let's begin to integrate our theory on latent heat fluxes into the context of a surface energy budget. An energy balance relation for the surface (assuming no net energy storage) can be written as:

$$R_n = \lambda_w E + H_{se} + H_G \quad (5.49)$$

Rearranging Equation 5.49 to solve for $\lambda_w E$, rearranging Equation 5.48 to solve for ΔT, and using substitution into Equation 5.49 to redefine H_{se}, we obtain:

$$\lambda_w E = R_n - (H_G + H_{se}) = R_n - \left(H_G + \frac{\rho_a c_p (\Delta T)}{r_h} \right) = R_n - \left(H_G + \frac{\lambda_w E \gamma^*}{s} \right) \quad (5.50)$$

After algebraic rearrangement the following expression is obtained:

$$\lambda_w E = \frac{s}{s + \gamma^*} (R_n - H_G) \quad (5.51)$$

Equation 5.51 represents the *diabatic component* of latent heat exchange. When combined with our previous expression for the adiabatic component, we obtain:

$$\lambda_w E = \underbrace{\frac{s}{s + \gamma^*} (R_n - H_G)}_{\text{Term I}} + \underbrace{\frac{\rho_a c_p (c_{wa}^*{}_{(Ta)} - c_{wa(Ta)})}{(s + \gamma^*) r_h}}_{\text{Term II}} \quad (5.52)$$

where Term I represents the diabatic component and Term II represents the adiabatic component. Equation 5.52 is the Penman-Monteith equation in final form, although sometimes it is written as:

$$\lambda_w E = \frac{s(R_n - H_G) + \rho_a c_p (c_{wa}^*{}_{(Ta)} - c_{wa(Ta)}) / r_h}{s + \gamma \dfrac{r_w}{r_h}} \quad (5.53)$$

which has the advantage of specifying both the water vapor and heat transport resistances. The Penman-Monteith equation carries the inherent condition of a balanced energy budget.

The Penman-Monteith equation can be related to the original Penman equation by recognizing: (1) that $1/r_h \approx \rho_a f(U)$, where $f(U)$ is an aerodynamic function dependent on windspeed (U), and $1/r_h$ therefore reflects an aerodynamic conductance for heat transport, (2) that $E_a = \rho_a f(U) (c_{wa}^* - c_{wa})$, where c_{wa}^* and c_{wa} are determined at air temperature, (3) using $\gamma \lambda_w = c_p$ for substitution, and (4) allowing for the use of γ^*, rather than γ to account for differences in the aerodynamic resistances to heat and water vapor transport.

Appendix 5.4 Derivation of the isothermal form of the Penman- Monteith equation

The Penman-Monteith model as written in Equations 5.52 and 5.53 contains an inherent feedback known as *radiative coupling*; as water is evaporated from the surface, and latent heat is carried away, the surface will cool. A cooler surface will radiate less long-wave energy, resulting in an increase in R_n, and thus an increase in $\lambda_w E$. This is a form of positive feedback on $\lambda_w E$. To eliminate the effect of radiative coupling the Penman-Monteith equation is often expressed in its *isothermal form* – i.e., defined in terms of equality between surface and air temperatures.

In deriving the isothermal form of the equation we recognize that *isothermal net radiation* (R_n^*) is defined as the net radiation that would be absorbed by a surface *if it existed at air temperature*. With respect to the surface energy budget, this requires re-expression of the Stefan-Boltzman radiant emission term ($\varepsilon_s \sigma T_s^4$, where ε_s is the emissivity of the surface with respect to long-wave radiation). The relationship between T_s and T_a is non-linear, meaning that a simple, first-order determination of T_a from a given T_s is not possible. Recall that we faced a similar mathematical complexity in our original derivation of the Penman-Monteith equation, when we sought to remove surface temperature (T_s) as a determinant of the water vapor concentration deficit. In that case, we used the Taylor Polynomial Theorem to estimate a linear relation between the saturation water vapor mole fraction (c_{wa}*) and air temperature (T_a) over a short range of temperature. Now, we will formalize this procedure by noting the general form of a Taylor expansion series as the first-degree polynomial: [$f(x) = f(c) + f'(c)\,(x - c)$]. Letting $T_s = x$, and $T_a = c$, and recognizing from elementary calculus that $dx^m = mx^{(m-1)}$, we can restate the relationship between surface temperature and radiant energy exchange as:

$$\varepsilon_s \sigma T_s^4 = \varepsilon_s \sigma T_a^4 + 4\,\varepsilon_s \sigma T_a^3 \left(T_s - T_a\right) \qquad (5.54)$$

once again assuming that $T_s - T_a$ is relatively small. If R_n^* is defined as:

$$R_n^* = (1 - r_s)\, R_S\, a_s + R_L + \varepsilon_s \sigma T_s^4 \qquad (5.55)$$

then the relationship between R_n^* and R_n can be expressed as:

$$R_n = R_n^* - 4\varepsilon_s \sigma T_a^3 (T_s - T_a) = R_n^* - 4\varepsilon_s \sigma T_a^3 (\Delta T) \qquad (5.56)$$

While some simplification has been accomplished in deriving Equation 5.56, it still contains a term for surface temperature; a fact with which we will need to reckon in the final solution.

Turning now to a path toward factoring the surface radiation-temperature feedback out of the original Penman-Monteith equation, we can write an isothermal analog of the energy budget equation ($R_n = \lambda_w E + H_{se} + H_G$) as:

$$R_n^* = \lambda_w E + \frac{(\rho_a c_p \Delta T)}{r_h} + H_G + 4\varepsilon_s \sigma T_a^3 \Delta T \qquad (5.57)$$

To simplify further algebraic manipulation, a term can be defined for the effective resistance of long-wave radiation emission (r_r):

$$r_r = \frac{\rho_a c_p}{4\varepsilon_s \sigma T_a^3} \qquad (5.58)$$

The term r_r is not a resistance in the same sense as has been used to define transport resistances. However, it satisfies the same conceptual aim of a 'diffusive resistance' in that it defines a mitigating factor that constrains flux. Note that r_r carries units of s m^{-1}, which is consistent with the units for r_h. Recognizing that: $1/r_h = (1/r_h + 1/r_r)$, we can write an isothermal form of the Penman-Monteith equation as:

$$\lambda_w E = \frac{s(R_n^* - H_G) + \rho_a c_p (c_{wa}^*{}_{(Ta)} - c_{wa(Ta)})(r_h^{-1} + r_r^{-1})}{s + \gamma \dfrac{r_w}{(r_h + r_r)}} \qquad (5.59)$$

This isothermal form of the Penman-Monteith equation retains an influence of surface cooling on G, the conductive flux of heat to deeper layers. In cases, where G is significant, this influence must be handled by independent accommodation of the altered temperature gradient between the surface and deeper layers.

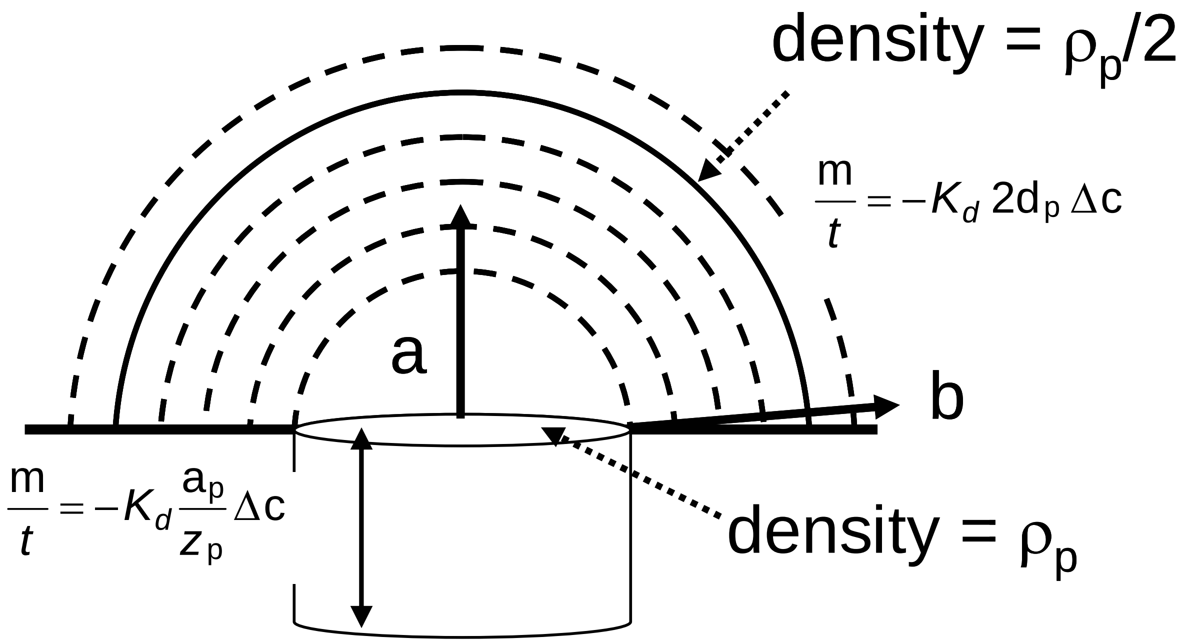

Figure 5.1. Scheme of diffusion through a pore and into the atmosphere above the pore. The flux rate of mass (m) per unit time (t) is dependent on Fick's law within the cylinder of the pore, and is linearly, directly dependent on the cross-sectional area of the pore (a_p) and the concentration gradient (Δc), and linearly, inversely dependent on the length of the pore (z_p). The flux rate (m/t) through the atmosphere above the pore is linearly, directly dependent on the diameter of the pore (d_p), not the cross-sectional area. The broken lines indicate contours of equal density and the solid curve indicates the spherical surface at which the density is equal to half that at the pore surface. The arrows labeled with a and b are of equal length, showing that the sharpest path through the density gradient is from the perimeter, outward at the lowest possible angle.

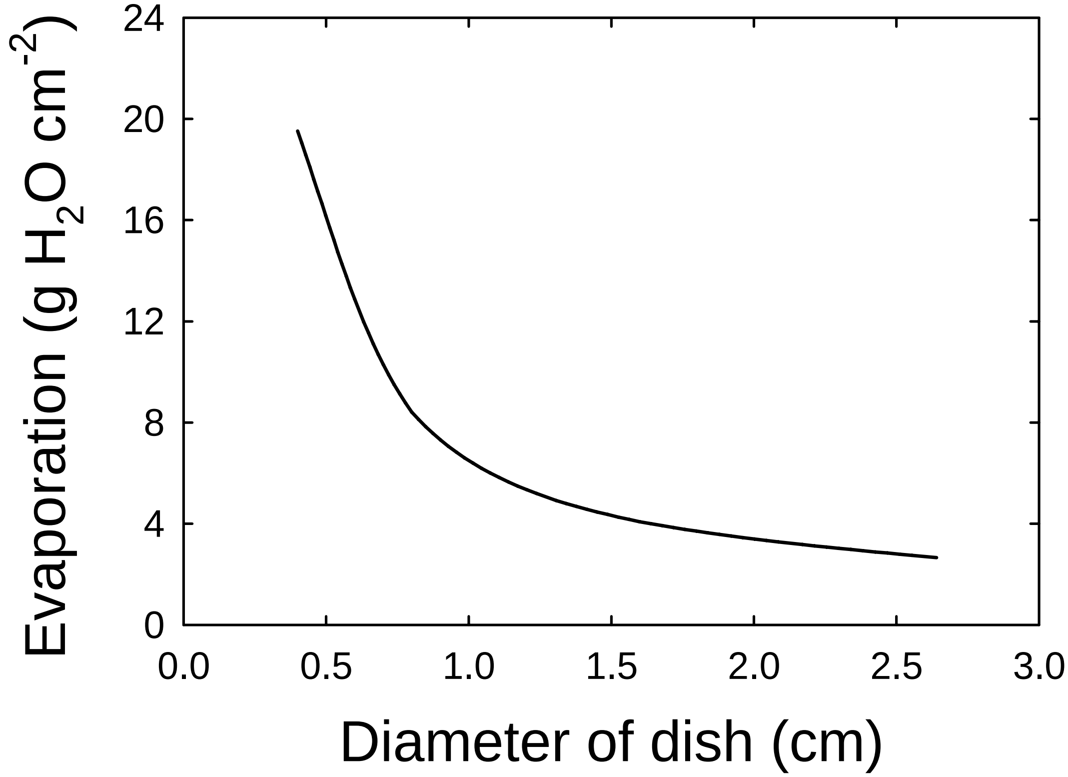

Figure 5.2. Evaporation rate into still air from dishes of open water of different diameter. From data provided in Sayre (1926).

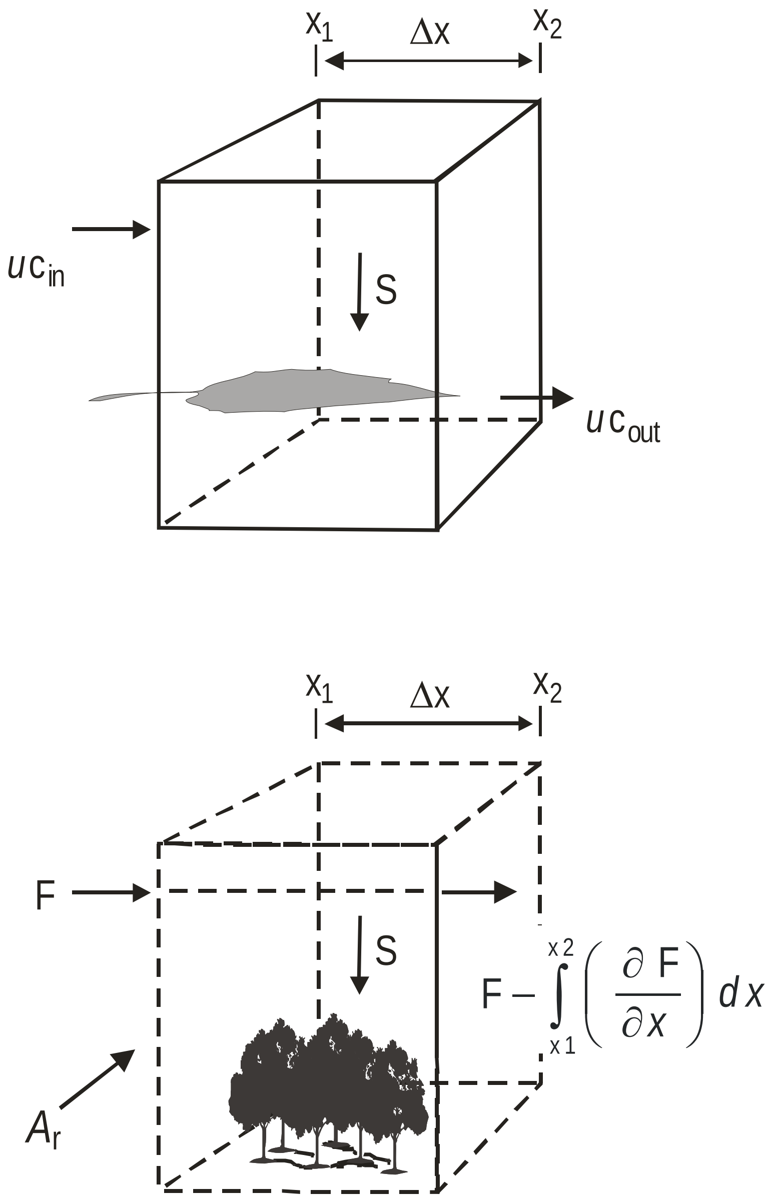

Figure 5.3. Volumes in which the principal of mass balance is illustrated. In the upper figure mass balance is applied to a leaf chamber in which the flux of a scalar into and out of the chamber is measured as the product between the flow rate (*u*) and concentration (c). In the lower figure mass balance is applied to a hypothetical volume representing the flux footprint for a stand of trees. In this case, the flux of the scalar occurs as the wind advects air through the volume. In the presence of a sink (S), flux divergence $\partial F/\partial x$ is produced.

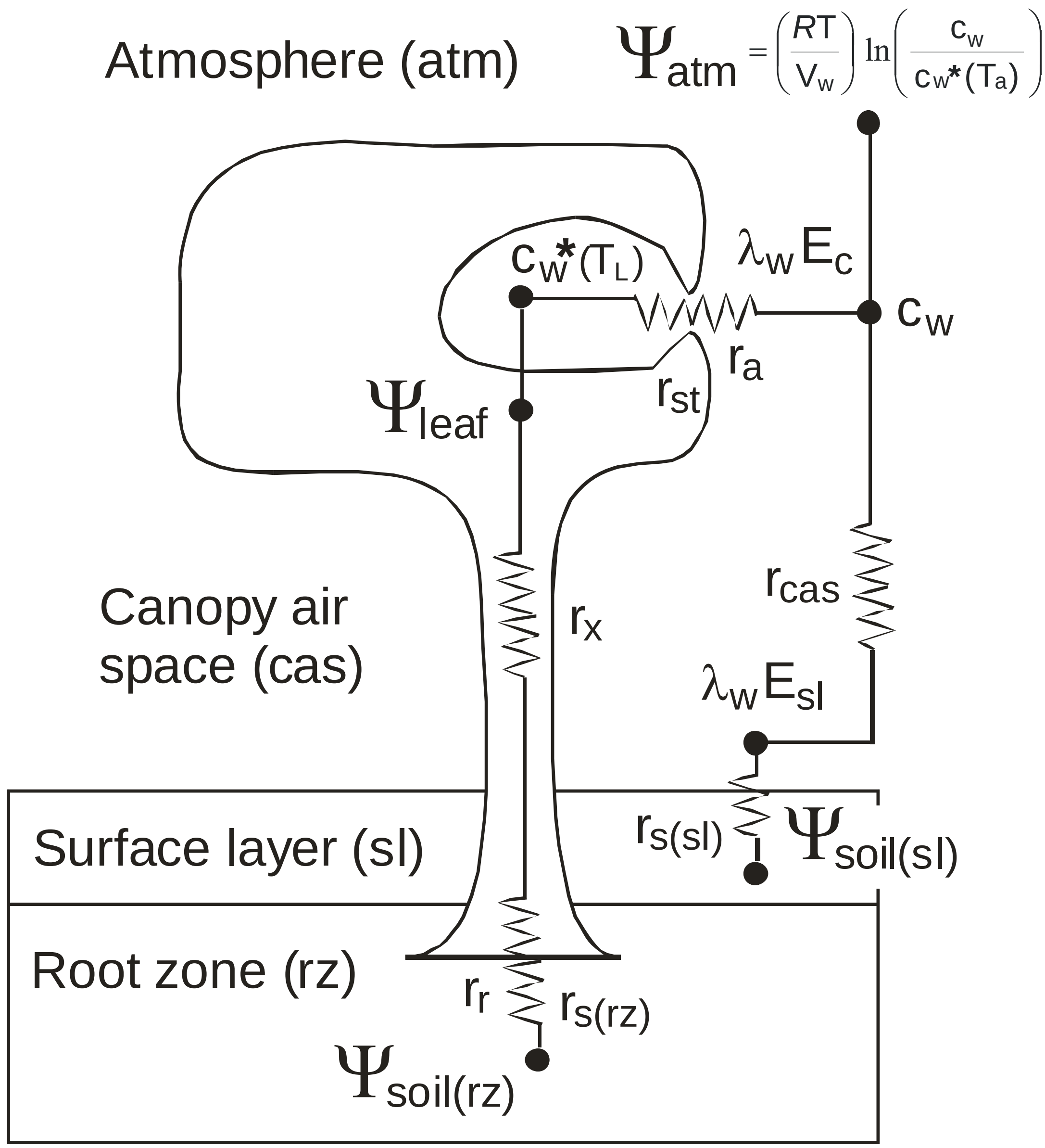

Figure 5.4. Schematic of water flux through the soil-vegetation-atmosphere continuum. The driving force for the flux is the water potential (Ψ_w) gradient between the soil and the atmosphere. Resistances along the path are depicted as electrical analog resistances for the soil (r_s), roots (r_r) xylem (r_x), stomata (r_{st}) and canopy air space (r_{cas}). Transpiration from the canopy is driven by the difference in saturated water vapor concentration at leaf temperature [$c_w^*(T_L)$] and water vapor concentration in the outside air (c_w). The model is adapted from that presented by Sellers et al. (1996b).

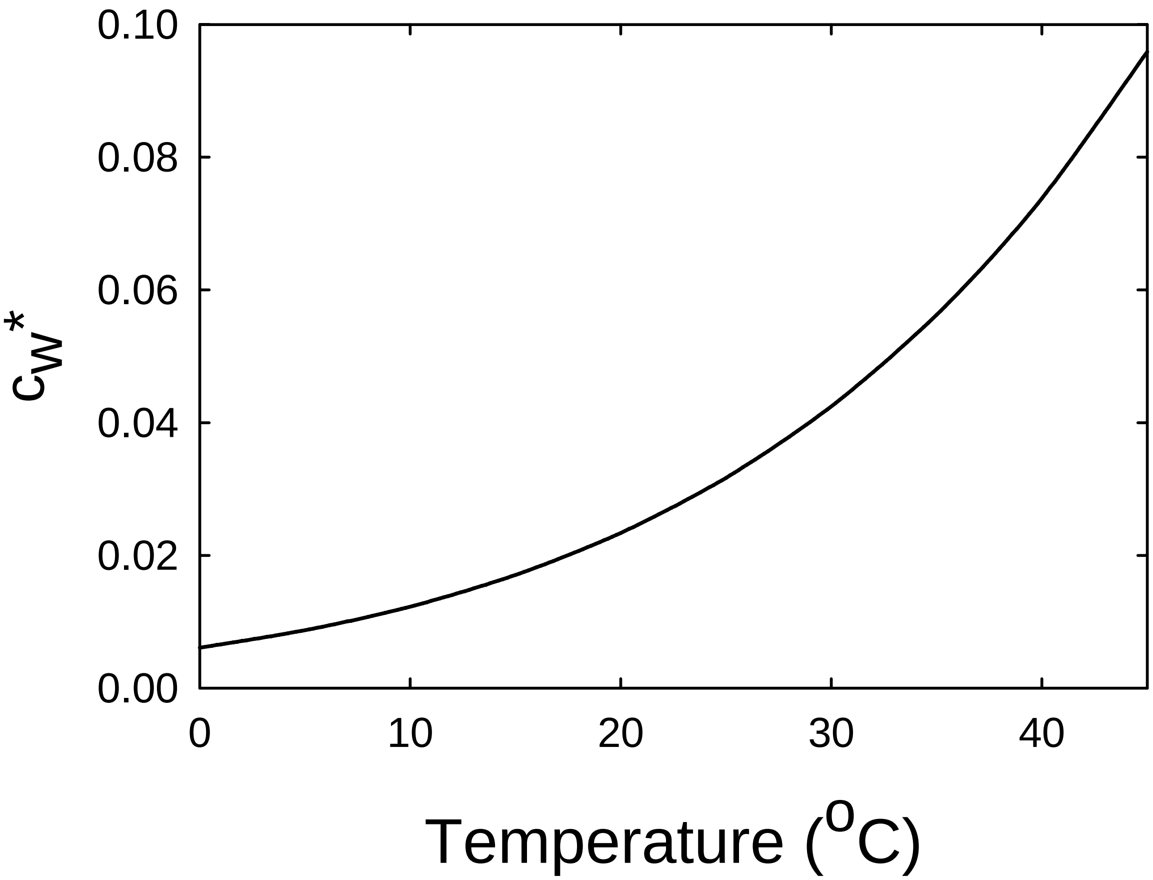

Figure 5.5 Relation between saturated water vapor mole fraction (c_w*) and temperature. The response surface was determined using Equation 5.16.

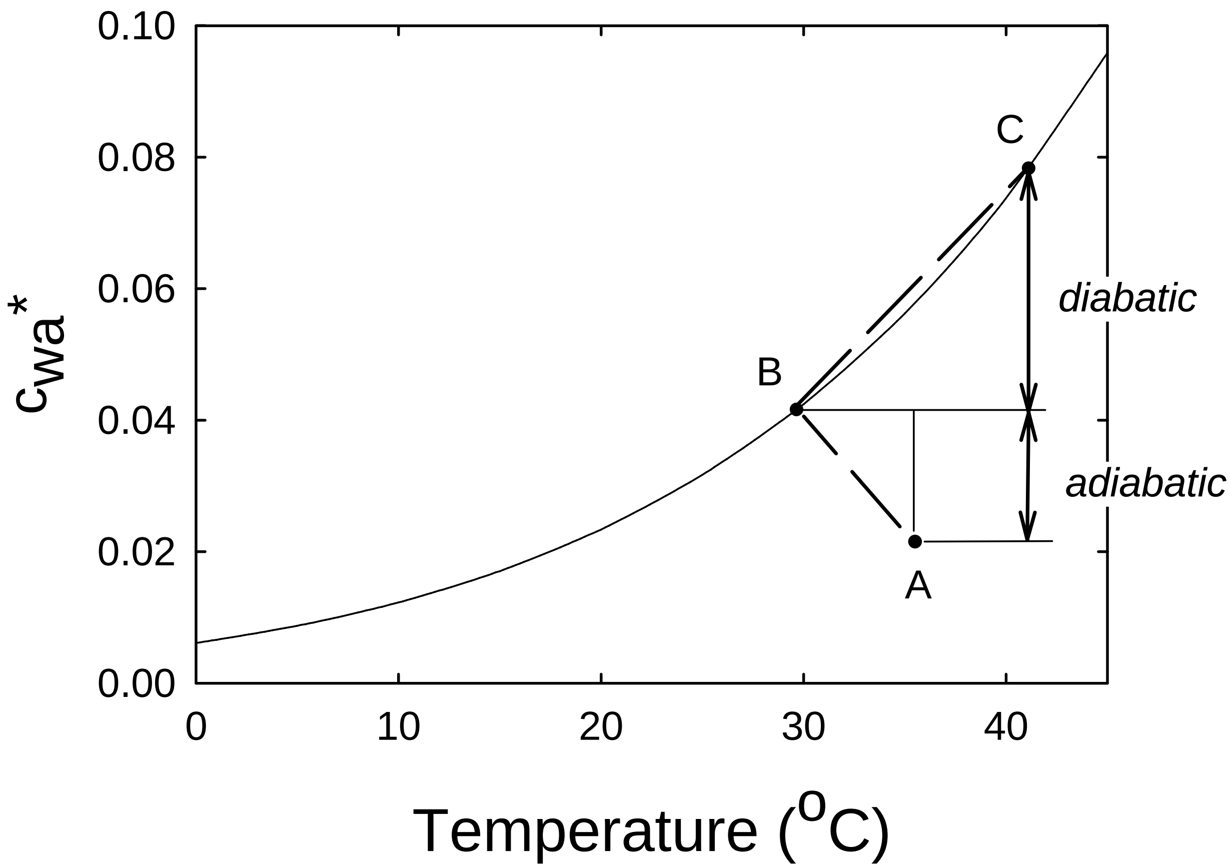

Figure 5.6. Partitioning of the increase in saturated water vapor mole fraction (c_{wa}*) as a function of air temperature into fractions due to adiabatic and diabatic energy exchange above a wet, evaporating surface. Developed from a concept presented in Monteith (1981).

Box 5.1 Photosynthetic Diffusive Relations at High Elevation

The partial pressure of an atmospheric constituent will decrease as elevation increases and, concomitantly, atmospheric pressure decreases. By Henry's Law, the concentration of CO_2 in the aqueous phase of the chloroplast (c_c) depends on the partial pressure of CO_2 in the intercellular air spaces (p_i), meaning that c_c should also decrease with increasing elevation. Numerous past studies have reported that plants at high elevation have adjusted to the lower c_c by increasing photosynthetic efficiency (Friend and Woodward 1990). In an early theoretical study, however, it was noted that the decrease in p_i due to an increase in elevation should be accompanied by an increase in the diffusion coefficient for CO_2 in air (K_d) (Gale (1972). In other words, although CO_2 becomes scarcer at high elevations, it also has more mobility when diffusing through air. Generally, K_d responds to atmospheric pressure (P) according to:

$$K_d = K_{d0}\left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)^2\left(\frac{\mathrm{P}_0}{\mathrm{P}}\right) \qquad \text{(B.5.1.1)}$$

where K_{d0}, T_0 and P_0 are the diffusion coefficient, temperature and pressure under standard conditions. The photosynthetic relations of high-elevation plants are made even more complex by the fact that most alpine plants occupy microhabitats near the ground where the air temperature can be several degrees higher than the air further above the ground. It is known that the Michaelis-Menten affinity coefficients of Rubisco for CO_2 (K_c) and O_2 (K_o) increase differentially with temperature (Jordan and Ogren 1984), and the Henry's Law coefficients for the solubility of CO_2 and O_2 in water decrease differentially with temperature (Edwards and Walker 1983). Given the complexity of these interactions, Terashima et al. (1995) used models of gas diffusion and photosynthetic biochemistry to estimate responses of photosynthesis rate to increases in elevation. The model predictions showed that reductions in p_i as elevation increased caused the gross photosynthesis rate (A_g) to decrease, even with consideration of the concomitant increase in diffusion coefficient. The greatest decreases in A_g occurred at the highest leaf temperatures.

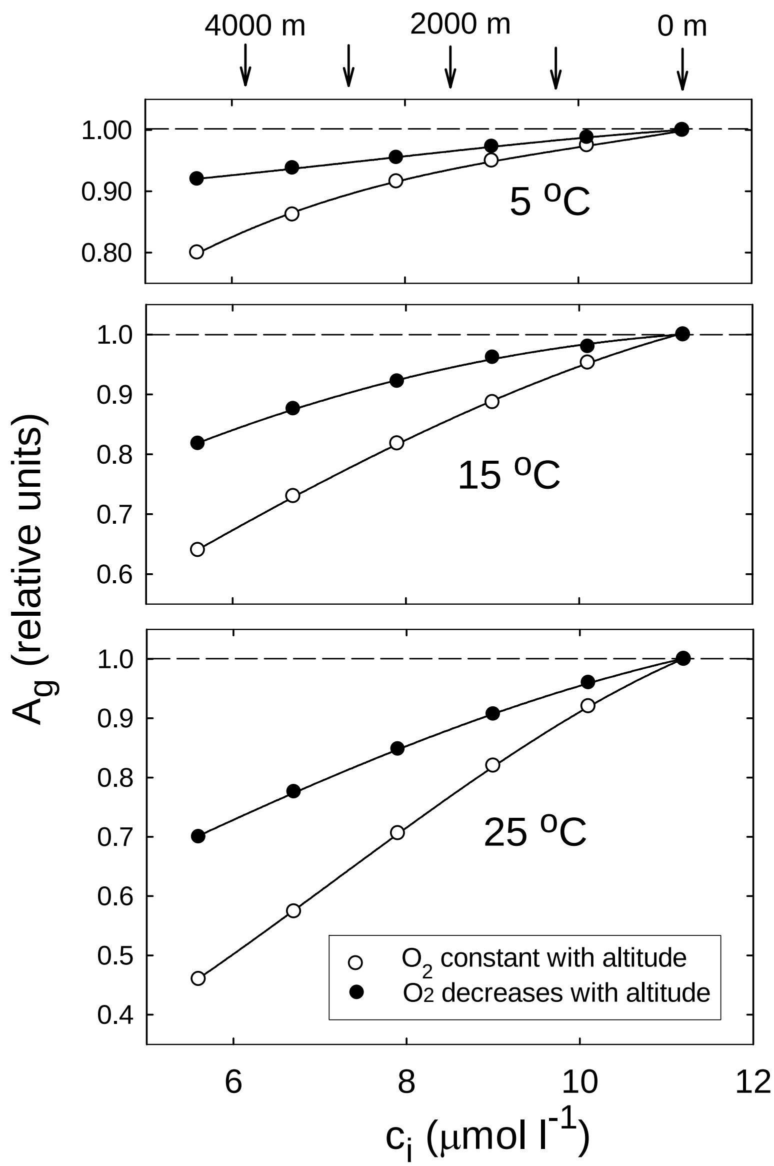

Figure B.5.1.1 The relationship between the intercellular CO_2 concentration (c_i) (in volumetric units) and gross photosynthesis rate (A_g) (expressed in relative units), at three leaf different temperatures. The results are from model calculations with two different scenarios; one in which the O_2 partial pressure remains constant as altitude increases, and one in which the O_2 partial pressure decreases as altitude increases. In both scenarios, CO_2 partial pressure was allowed to decrease with altitude. Altitude that corresponds to c_i is shown across the top axis. Redrawn from Terashima et al. (1995).

Footnotes (Chapter 5)

[1] The mean free path (λ_p) of individual molecules in a gas mixture is determined as: $\lambda_p = 1/\rho\pi d^2$, where ρ is density of the molecule in the gas phase and d is the molecule diameter. Most of the molecules in air are N_2, which has a molecular diameter of 0.15 nm; H_2O molecules have a diameter of 0.28 nm. The estimated λ_p of air is approximately 0.8 µm; the λ_p for water vapor alone is lower, since its diameter is higher, and is approximately 0.6 µm.

[2] The units of free energy and water potential can be reconciled if we consider that $1\ J = 1\ m^2\ kg\ s^{-2}$, and pressure is expressed as force per unit area, or $1\ N\ m^{-2} = 1\ m\ kg\ s^{-2}\ m^{-2}$; the final relationship between the two is $\psi_w = G\ V_w^{-1}$, where V_w^{-1} is the partial molal volume of pure water, or $18 \times 10^{-6}\ m^3\ mol^{-1}$.

[3] The negative water potential produced by addition of a solute should not be equated with the negative ΔG of an exergonic reaction. In the case of water potential, as values get more negative, they reflect *lower free energy relative to pure water*.