

Wood in the stationary state: Zero entropy gradients for water vapor and bound water

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Summary. According to nonequilibrium thermodynamics, the local rate of entropy production is minimized for moist wood in the stationary state. Furthermore, the rate of entropy production due to moisture flow must be zero in this state. Conservation of energy applied to the steady flow of water vapor through an arbitrarily selected volume element of wood shows that the vapor entropy gradient is zero. Because the entropy production due to moisture flow must be balanced by a corresponding entropy flow away from the element, entropy gradients for bound water and water vapor are equal and the bound water entropy gradient also is zero.

Introduction

Nonequilibrium thermodynamics show that for stationary-state systems (systems in which matter flux is zero but heat flux is nonzero due to a fixed temperature gradient), fluxes conjugate to the unrestrained (or nonfixed) driving forces are zero. In the Choong (1963) stationary-state experiments, the wood samples were sealed and fluxes of moisture and air to the surroundings were zero. A constant temperature difference was applied externally, but chemical potentials just inside the boundaries of each sample freely assumed values consistent with the initial moisture content and imposed temperature distribution. In addition, calculations for the Choong data suggested that entropy gradients for both bound water and water vapor were essentially zero (Nelson 1986). Adoption of this concept has made possible the quantification of molar heats of transfer in thermodynamic models of moisture transport (Nelson 1989). Analytical verification of the zero-entropy-gradient result would strengthen the credibility of these models.

It is noteworthy that zero matter fluxes are not determined by zero values of the driving forces, but by the requirement that the local rate of entropy production be minimized (Katchalsky, Curran 1965). The theory also shows that the local rate of entropy production due to matter flow must be zero because the matter flow is zero. To consider entropy production alone, however, is to consider only part of the governing process. The purpose of this paper is to show that zero entropy gradients for water vapor and bound water are required by the conservation of energy and by a balance between entropy production and entropy outflow in an arbitrarily chosen volume element of wood.

Zero matter flux

A combined flux of water vapor and sorbed water equal to zero for wood in the stationary state is derived in this section using a modification of the analysis described by Katchalsky and Curran (1965). The wood-water system is heterogeneous because water occurs in two states; air also is present in cell cavities within the wood. In the present analysis, local chemical potentials of the bound water and water vapor and local temperatures of all three phases are considered equal. If chemical, electrical, viscous, and gravitational effects are absent, the rate of entropy production in a volume element due to flows of energy, sorbed water, and water vapor may be written as

$$\sigma = J_q X_q + J_s X_s + J_v X_v \quad (1)$$

where $X_q = d(1/T)/dx = -(1/T^2)(dT/dx)$, $X_s = -d(\mu_s/T)/dx$, and $X_v = -d(\mu_v/T)/dx$. This equation includes contributions of all three phases to the total entropy production in the element. It is approximate, however, because the contribution of air to σ is assumed to be negligible. This approximation is valid at temperatures below 50°C for which the total pressure remains close to atmospheric, the mole ratio of vapor to air is small, and the velocity ratio of vapor to air is large. Quantities X_q , X_s , and X_v denote driving forces for transport of energy, sorbed water, and water vapor; J_q , J_s , and J_v are the corresponding fluxes on a volume of wood basis. Quantity T is the Kelvin temperature, and μ_s and μ_v refer to the chemical potentials of sorbed water and water vapor. Because $\mu_s = \mu_v$, the phenomenological equations describing the system may be written in the form

$$\begin{aligned} J_q &= L_{qq} X_q + L_{qw} X_w \\ J_w &= L_{wq} X_q + L_{ww} X_w \end{aligned} \quad (2)$$

where $X_w = X_s = X_v$ and $J_w = J_s + J_v$ (Nelson 1989). This abbreviated form of the equations expresses the fluxes and forces as independent quantities. The phenomenological coefficients L_{qq} and L_{ww} are related to the conductivities for uncoupled heat and moisture transfer in the wood. The terms L_{qw} and L_{wq} are cross coefficients expressing effects of coupling between the processes of energy and moisture flow. Summing of J_s and J_v implies that the steady-state flows determining the combined flux J_w occur along parallel pathways. The cell cavity (including the pit chamber) is taken to be in series with the parallel combination of cell crosswalls, pit membrane, and pit membrane pores. Flows through continuous sidewalls of the cell and through the pit membrane are considered negligible due to the length of continuous sidewalls and the small membrane area relative to the crosswall area. Thus, the governing parallel flows are bound water diffusion through cell crosswalls and hindered water vapor diffusion through pit membrane pores (Nelson 1989). The simple summing of fluxes is expected to describe, for practical purposes, all instances of steady transverse diffusion in wood. The local entropy production rate becomes

$$\sigma = J_q X_q + J_w X_w \quad (3)$$

and substitution of J_q and J_w from Eqs. (2) yields

$$\sigma = L_{qq} X_q^2 + 2 L_{wq} X_q X_w + L_{ww} X_w^2 \quad (4)$$

due to the Onsager reciprocal relation, $L_{qw} = L_{wq}$ (Skaar 1988).

During the approach to the stationary state in the Choong experiments, local values of X_q rapidly became fixed quantities, but X_s and X_v (and hence X_w) freely assumed values determined by the initial moisture content and imposed temperature difference. According to the principle of minimum entropy production, σ takes on a minimum value upon attainment of the stationary state (Katchalsky, Curran 1965). Thus, for constant X_q and for L_{qq} , L_{wq} , and L_{ww} independent of X_q and X_w ,

$$\partial\sigma/\partial X_w = 2 L_{wq} X_q + 2 L_{ww} X_w = 2 J_w = 0$$

$$J_w = J_s + J_v = 0 \quad (5)$$

$$J_s = -J_v = \text{constant} .$$

This result indicates a possible circulation of bound water and water vapor within the wood. Whether this cyclical process occurs, or fluxes J_s and J_v are identically zero, is not clear. The principle of microscopic reversibility, which forbids cyclical processes under conditions of thermodynamic equilibrium ($\sigma = 0$), does not apply to the non-isothermal conditions ($\sigma > 0$) considered here (Rice 1967). Thus, the rate of entropy production due to the combined moisture flow is zero [$J_w = 0$ in Eq. (3)], but the entropy production associated with individual fluxes J_s and J_v remains undetermined.

Flows of entropy and energy

A key requirement for attainment of the steady or stationary state is that the rate of entropy flow away from any volume element in the wood equal the rate of entropy production in the element (Katchalsky, Curran 1965). If flow is one-dimensional, this balance may be expressed as

$$\sigma = dJ_e/dx \quad (6)$$

where J_e is the entropy flux in the x direction. For conditions of the Choong experiment, the flux equation given by these authors is

$$J_e = J_q/T - J_s (\mu_s/T) - J_v (\mu_v/T) = J_q/T - J_w (\mu_w/T) = J_q/T \quad (7)$$

where J_q is the total energy flux. Equation (7) shows that J_e is determined by the energy flux and temperature when $J_w = 0$. Furthermore, it can be shown that J_q is constant throughout wood in the steady or stationary state. Differentiation of Eq. (7) with respect to x gives

$$dJ_e/dx = (1/T) (dJ_q/dx) + J_q X_q + J_w X_w \quad (8)$$

and comparison with Eqs. (3) and (6) shows that

$$dJ_q/dx = 0 . \quad (9)$$

Thus, energy is conserved in either the steady or stationary state because J_q is independent of x even when J_w is nonzero.

S. R. de Groot (1966) has shown that, under certain conditions, irreversible processes may be described in different frames of reference and that the Onsager reciprocal relations and the form of the phenomenological equations remain valid for a transformation to new variables. These conditions require that the new variables be

conjugate variables (dimensions of each product of flux and force in the transformed expression for σ are those of a volumetric rate of entropy production). Equations (1)–(9) describe a system in which entropy and energy fluxes are defined relative to the zero velocity of the volume element. It is convenient, however, to write Eqs. (1), (2) and (7) in a different frame of reference, in which the fluxes of total entropy and energy are referenced to the entropy and energy fluxes due to moisture flow. Thus, the entropy and energy fluxes differ from those in the old system, but the entropy production, entropy flow, and moisture fluxes remain unchanged. Let quantities in the new system of reference be denoted by primed symbols. Then a new energy flux, related to J_q , is defined as

$$J'_q = J_q - J_s h_s - J_v h_v = J_q - J_s (h_s - h_v) = J_q - J_s T (s_s - s_v) \quad (10)$$

through use of the equilibrium relation $h_s - h_v = T (s_s - s_v)$. Flux J'_q is called the reduced heat flow, and represents the amount by which J_q exceeds the sum of the mean energy fluxes due to flow of sorbed water and water vapor. Quantities s_s and s_v are entropies per mole of sorbed water and water vapor; h_s and h_v are the corresponding enthalpies. Similarly, a new entropy flux may be defined in terms of J_e from Eq. (7) and Eq. (10) as

$$J'_e = J'_q/T = J_q/T - J_s (s_s - s_v) = J_e - J_s (s_s - s_v) \quad (11)$$

and regarded as a reduced flux indicating the amount by which the total entropy flux exceeds the entropy flux due to moisture flow. Other variables in the new system may be written as follows:

$$\begin{aligned} J'_s &= J_s; & J'_v &= J_v \\ X'_q &= -(1/T^2) (dT/dx) = X_q \\ X'_s &= -(1/T) (\partial\mu_s/\partial x)_T = X_s + h_s X_q \\ X'_v &= -(1/T) (\partial\mu_v/\partial x)_T = X_v + h_v X_q \end{aligned} \quad (12)$$

where X'_s differs from X'_v . The phenomenological equations in the new frame of reference take the form

$$\begin{aligned} J'_q &= L'_{qq} X'_q + L'_{qs} X'_s + L'_{qv} X'_v \\ J'_s &= L'_{sq} X'_q + L'_{ss} X'_s + L'_{sv} X'_v \\ J'_v &= L'_{vq} X'_q + L'_{vs} X'_s + L'_{vv} X'_v \end{aligned} \quad (13)$$

so two independent driving forces X'_s and X'_v characterize water flow in the system, rather than the single force X_w in Eqs. (2). Of more interest, however, is the rate of entropy production, σ' , given by

$$\sigma' = J'_q X'_q + J'_s X'_s + J'_v X'_v. \quad (14)$$

Substitution of Eqs. (10) and (12) into Eq. (14) produces

$$\sigma' = J_q X_q + J_s X_s + J_v X_v, \quad (15)$$

an equation identical to Eq. (1). Thus, from Eqs. (1) and (15),

$$\sigma = \sigma' \quad (16)$$

in agreement with the concept of a unique rate of entropy production. This invariance in entropy production implies that volumetric flows of entropy also are invariant because of the balance between them given by Eq. (6). Moreover, Eq. (11) shows that the fluxes J_e and J'_e are not equal unless $s_s = s_v$ or $J_s = 0$. The entropy flows (x derivatives of J_e and J'_e) must be invariant, however, implying that the fluxes differ at most by a constant.

Heats of transfer

The rate of entropy flow from a volume element of wood in the stationary state may be written, using Eqs. (7) and (10), as

$$dJ_e/dx = d(J_q/T)/dx = (1/T)(dJ'_q/dx) + J'_q X_q + J_s [d(s_s - s_v)/dx]. \quad (17)$$

From Eqs. (9) and (10),

$$dJ_q/dx = 0 = dJ'_q/dx + J_s [d(h_s - h_v)/dx] \quad (18)$$

where the gradient in enthalpy difference may be obtained from

$$h_s - h_v = \mu_s + T s_s - h_v. \quad (19)$$

Differentiation of Eq. (19) gives

$$\begin{aligned} d(h_s - h_v)/dx &= d\mu_s/dx + T(ds_s/dx) + (s_s - c_{pv})(dT/dx) \\ &= -[(Q_s^*/T) + c_{pv}](dT/dx) + T(ds_s/dx). \end{aligned} \quad (20)$$

Quantity Q_s^* denotes the heat of transfer for bound water diffusion and c_{pv} the molar heat capacity of water vapor. Equation (20) is written using the following relationships:

$$dh_v/dx = c_{pv}(dT/dx) \quad (21)$$

$$J_w = 0 = -(L_{ww}/T) \{[(Q_s^*/T) + s_s](dT/dx) + d\mu_s/dx\} \quad (22)$$

where Eq. (22) describes the steady combined flow of bound water and water vapor in wood. This equation originates in Eqs. (2) from the definition $U^* = [J_q/J_w]_{X_q=0} = Q_s^* + h_s = L_{qw}/L_{ww} = L_{wq}/L_{ww}$, where U^* is the energy of transfer (de Groot 1966). This energy is the average energy transferred due to the combined flow of one mole of moisture under isothermal conditions, and is expressed here in terms of the sorbed water. Thus, U^* is composed of the average energy of the sorbed water (h_s) and the increment of average energy that must be acquired for the sorbed water to participate in diffusion (Q_s^*). Substitution of $L_{wq} = L_{ww}(Q_s^* + h_s)$ into the J_w relationship in Eqs. (2) leads to Eq. (22) if X_w is taken as $-d(\mu_s/T)/dx$. In the stationary state, however, $J_w = 0$. Quantity L_{ww} ($= L_{ss} + L_{vv}$) is a phenomenological coefficient representative of the combined flow. Symbols L_{ss} and L_{vv} refer to phenomenological coefficients for the separate flows. Substitution of Eqs. (10), (18), and (20) into Eq. (17) gives

$$dJ_e/dx = J_q X_q - J_s (Q_s^* + h_s - h_v + c_{pv} T) X_q - J_s (ds_v/dx) = J_q X_q. \quad (23)$$

The right side of this equation follows from Eqs. (8) (for $J_w = 0$) and (9), and shows that the sum of the multipliers of J_s must be zero. From the equation for the entropy

of water vapor (considered an ideal gas), the vapor entropy gradient is

$$ds_v/dx = (c_{pv}/T) (dT/dx) - R (d \ln p/dx) \quad (24)$$

where p is the vapor pressure. Substitution into Eq. (23) yields

$$d \ln p/dT = -(Q_s^* + h_s - h_v)/RT^2. \quad (25)$$

A different heat of transfer may be defined as

$$Q_v^* = Q_s^* + h_s - h_v \quad (26)$$

leading to a restatement of Eq. (25) as

$$d \ln p/dT = -Q_v^*/RT^2. \quad (27)$$

Denbigh and Raumann (1951) refer to Q_v^* as an overall heat of transfer.

Conservation of energy and zero entropy gradients

The argument can be made that entropy gradients for sorbed water and water vapor must be zero because $J_w = 0$ in the stationary state. In this case, the flux of energy J_q in Eq. (3) reduces to a pure heat flux and the entropy production (or irreversibility) in an arbitrary volume element of wood is due to heat conduction alone. In view of Eqs. (5), however, the element must be regarded as an open system capable of exchanging both matter and energy with its surroundings. Because all three phases making up the element satisfy the requirements of a pure substance, conservation of energy applies to each phase separately. Entropy gradients may be evaluated, however, by analyzing the gas phase only. The analysis shows that the conservation of energy is satisfied separately for each component of the phase (air or water vapor) when the individual flows are steady. Thus, the energy equation for steady flow of water vapor may be written as

$$du_v = dq - dw \quad (28)$$

where u_v is the molar internal energy (also the total energy because changes in kinetic and potential energy are assumed negligible), and dq and dw are the net heat absorbed from the surroundings and work done by the vapor per mole of vapor transferred (Lee, Sears 1963). The work done is that required to displace a mole of vapor within the element and is $dw = d(p v)$, where v is the molar volume. Eq. (28) applies to open or closed systems because du_v , dq , and dw are intensive variables. Enthalpy h_v is defined as $u_v + p v$, and division of Eq. (28) by T gives

$$dq/T = d(u_v + p v)/T = dh_v/T \quad (29)$$

where dq/T may be interpreted as a change in vapor entropy due to entry of a mole of vapor into the element and subsequent outflow at a lower temperature. The transported energy in excess of the enthalpy of the entering vapor (not considering heat conduction in the vapor) is defined as a heat of transfer (de Groot 1966) and denoted here as Q_v^* . The flow is from a warmer to a cooler region and these regions differ in temperature by dT , so the net absorbed heat may be expressed in terms of

the entropy change due to vapor flow as

$$dq = T \{ [Q_v^*/(T + dT)] - [Q_v^*/T] \} = -(Q_v^*/T) dT \quad (30)$$

if it is assumed that Q_v^* is constant and dT is small in comparison with T (Denbigh 1951). Combination of Eqs. (21), (29), and (30) leads to

$$Q_v^* = -c_{pv} T \quad (31)$$

indicating that, within the element, a vapor entropy increase due to a change in state (dh_v/T) is balanced by the entropy decrease associated with vapor flow ($-dq/T$). Combination of Eqs. (24), (27), and (31) shows that

$$ds_v/dx = 0. \quad (32)$$

Thus, conservation of energy requires zero vapor entropy change within the element.

The bound water entropy gradient also is calculable because the two entropy fluxes discussed earlier differ by only a constant. Invariance of the entropy flows derived from Eq. (11) yields

$$d(J_e - J'_e)/dx = 0 = J_s [d(s_s - s_v)/dx] \quad (33)$$

leading to equality of the entropy gradients given by

$$ds_s/dx = ds_v/dx. \quad (34)$$

Thus, Eqs. (32) and (34) show that

$$ds_s/dx = 0. \quad (35)$$

It is noted that introduction of Eq. (31) into Eq. (26) gives

$$Q_s^* = h_v - h_s - c_{pv} T = Q_v + Q_w - c_{pv} T \quad (36)$$

where Q_v and Q_w are the heat of vaporization and differential heat of sorption of liquid water, respectively. Thus, Eqs. (31) and (36) agree with previous formulations of Q_v^* and Q_s^* based on a zero vapor entropy gradient inferred from calculations of s_v (Nelson 1986, 1989).

The zero entropy gradients in Eqs. (32) and (35) are due to conservation of energy and to a balance between entropy production in any wood volume element and flow of entropy away. For moisture flow, the zero entropy production must be balanced by zero entropy flow, and this is possible only when the entropy gradients are zero.

Conclusion

For moist wood in the stationary state, the combined flux of bound water and water vapor and the individual entropy gradients for each moisture phase must equal zero. Zero moisture flux ensures a zero entropy production rate due to moisture flow; conservation of energy and a balance between production and flow of entropy ensure constant entropies for each phase. This result is intuitively satisfying, for if there is to be zero entropy production due to moisture flow, as theory predicts, constant entropies for the moisture are expected.

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(Received October 22, 1990)

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