THERMAL MIGRATION IN BIOLOGICAL TRANSPORT?

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ABSTRACT It is shown by thermodynamic arguments and by semiquantitative considerations that the contribution of thermal migration to biological transport is likely to be small.

Spanner [1, 2] has suggested that local temperature gradients resulting from the unequal distribution of metabolic activity may be a major cause of biological transport, particularly that of water in plants. This view has not received much attention, but in view of a more recent, equivocal, discussion of the idea [3], I wish to try and clarify the relation between thermal migration and biological transport although I can add nothing to what is implied in the theoretical monographs of Denbigh [4] and de Groot [5].

We can, in general, ascribe water transport through a system to the maintenance by any means of a gradient of the chemical potential of water, but when considering such a system it may seem easier to find first the conditions under which a balanced state of zero net water flow can be achieved, and so deduce that by altering the conditions a flux of water will arise. Thus Spanner used the Gibbs equation (which relates the vapor pressure of a liquid to the applied pressure) and the Clapeyron-Clausius equation to find that pressure which must be applied to the surface of the colder of two separate volumes of water in order to equalize their vapor pressures. Spanner postulated a device which allowed both the application of this pressure and the equilibration of the vapor by distillation, but he avoided the apposition of the two liquid regions at a membrane. He thereby neglected the particular transport process which he was trying to elucidate. To explore his approach more thoroughly I have therefore derived an equation for the "thermal osmotic pressure" between two aqueous phases connected through a membrane permeable to water. Since Spanner's result is independent of the presence of solute, we shall consider an osmometer in which water alone is present.

A rigid permeable membrane at the bottom of a U tube separates water at temperature, T, in a tall limb I from water at $T + \Delta T$ in limb II. The corresponding vapor pressures are p_{I} and p_{II}. Limb I is filled until the hydrostatic pressure difference, π, exerted at the membrane is such that flow through the membrane ceases. In a virtual transfer of the molar volume, V, from I to II, the work done on the system is πV. This is equated to the work done by the system when the same quantity of water is transferred reversibly from II to I through the vapor. This transfer comprises a vaporization at p_{II}, a reversible adiabatic expansion to that intermediate pressure, p, which is reached at temperature T, an isothermal adjustment to pressure p_{I}, and finally a condensation at p_{I}. The work equation is:

$$\pi V = R(T + \Delta T) + C_v \Delta T + RT \ln \frac{p}{p_{\mathrm{I}}} - RT$$

where C_v is the specific heat of the vapor at constant volume. We substitute the relation $C_v = R/(\gamma - 1)$, introducing γ, the ratio of the specific heats of the vapor. We expand the adjustment term,

$$RT \ln \frac{p}{p_{\mathrm{I}}} = RT \left(\ln \frac{p}{p_{\mathrm{II}}} + \ln \frac{p_{\mathrm{II}}}{p_{\mathrm{I}}} \right)$$

and substitute in it the Clapeyron-Clausius equation in the form

$$\ln \frac{p_{\mathrm{II}}}{p_{\mathrm{I}}} = L\Delta T/RT^2$$

which shows the independence of vapor pressure on L, the latent heat of vaporization. We also substitute in the adjustment term the relation for an adiabatic expansion, subject to the convenient approximation that $\Delta T \ll T$:

$$\ln \frac{p}{p_{\mathrm{II}}} = \frac{\gamma}{\gamma - 1} \ln \left(\frac{T}{T + \Delta T} \right) \simeq \frac{-\gamma \Delta T}{(\gamma - 1)T}$$

The work equation finally reduces to:

$$\pi V = L\Delta T/T \tag{1}$$

This is the same as Spanner's result, and it implies that π is about 7×10^4 cm H_2O/°C.

However, this treatment is unsatisfactory in a number of ways. The sum of the two isothermal entropy changes is negative, which shows that the cycle includes an irreversible process; clearly this must occur in the membrane. The cyclic treatment also implies that, in the transfer from I to II, osmotic work is converted into heat; or in other words, that an amount of heat, L, is carried across the membrane when the transfer of volume, V, is made. When we compare equation (1) with equation (11) of Denbigh [4], derived for the thermal migration of a gas through a membrane, we find them to be identical if Denbigh's heat of transport can have the value L. This seems to be possible in our system only on the unrealistic postulate that the membrane is permeable only to water vapor. This lack of reality is enhanced by the tacit assumption we have been making that a sharp discontinuity of temperature ΔT exists; we have thus restricted energy transfer to that amount, L, carried by the vapor, whereas any real membrane must also conduct heat as a result of the difference of temperature between its surfaces.

We should therefore see whether thermal migration in the temperature gradient in the membrane can be successfully treated by the methods of irreversible thermodynamics. We modify de Groot's treatment of thermal diffusion in order to apply it to thermal migration of component 1 through a membrane consisting of component 2. Such migration is an example of thermal osmosis, and there is little evidence for it in two-component systems [6]; however, the present approach could be extended to multicomponent systems if required.

The fundamental differential equation for the flux J_1 of component 1 at weight fraction c_1 through a plane of the membrane is:

$$J_1 = -D \operatorname{grad} c_1 - D'c_1(1 - c_1) \operatorname{grad} T \tag{2}$$

where D is the diffusion coefficient, and D' is the thermal diffusion coefficient. The relation between these coefficients introduces Q^*_1 the specific heat of transfer, and the partial specific enthalpies h_1 and h_2:

$$(Q^*_1 - h_1 + h_2)/RT = D'T/D \tag{3}$$

The heat of transfer is defined by de Groot as the amount of heat carried per unit weight of 1 migrating through the plane at uniform temperature, and therefore differs slightly from the heat of transport defined by Denbigh. The difference $h_2 - h_1$ will generally be small.

Study of thermal diffusion in solutions, for example by Snowdon and Turner [7], has shown that Q^* for most solutes is positive and small compared with the mean thermal energy; usually the ratio of equation (3) is less than 0.3. We see from equations (2) and (3) that when Q^*_1 is positive, the flow of component 1 occurs down the temperature gradient. Denbigh and Raumann [8] in their experimental studies of thermal osmosis of gases through membranes found negative values of Q^* of a few kilocalories: among the factors advanced to explain these results was that, perhaps as a result of loss of degrees of freedom of motion, the gas has a positive heat of solution in the membrane, which corresponds with a negative heat of transfer across the gas-membrane interface. Similarly, negative values of Q^*_1 are conceivable in biological membranes.

Metabolism keeps cells at a higher temperature than their surroundings; if thermal migration is to account for active transport into a cell, Q^*_1 must therefore be negative, and the second term of equation (2) must far outweigh the first. We have enough information to decide whether this can be so. On the basis of the following rough calculation, I doubt the claim [3] that a value of 10^3 °C/cm is reasonable for the temperature gradient across the cell wall. Consider a spherical cell characterised by: $Q_{O_2} = 10$; dry wt/wet wt $= 0.2$; radius $= 7.5 \times 10^{-4}$ cm. We take the thermal conductivity of paraffin wax, 0.6×10^{-3} cal cm/cm^2 second °C, as appropriate to a lipoid membrane, while noting that the conductivity of water is only about 2.5 times as great; we assume 1 ml $O_2 = 5$ cal; and that the cell has a density of 1.0. Since the ratio of volume to surface area is (radius/3) we have

$$\text{grad } T = \frac{\text{radius} \times \text{heat production/ml second}}{3 \times \text{thermal conductivity}}$$

so that

$$\text{grad } T = \frac{7.5 \times 10^{-4} \times 5 \times 10 \times 0.2}{3 \times 0.6 \times 10^{-3} \times 60 \times 60} = 1.2 \times 10^{-3} \text{ C/cm.}$$

This low temperature gradient makes it unlikely that the second term of equation (2) outweighs the first, but supposing that it did, differentiation shows that $\partial J_1/\partial T$ has the same sign as Q^*_1, and therefore the rate of active transport, which has a positive temperature coefficient, cannot be determined by thermal migration.

I believe this argument shows, as foreshadowed by Mitchell [3], that thermal migration can make only a trivial contribution to biological transport.

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