

by any influences such as meteorites or vulcanism there may be buried oxidized rock containing ferric iron.

We apply the same reasoning to Mars which also has no magnetic field and thus is potentially subject to solar wind contact, although the presence of a light atmosphere on Mars (6), perhaps 1 percent of that on Earth, will cause the wind to be deflected by the ionosphere and thus avoid capture to some extent. If there had been no atmosphere, Mars would have had to put out enough water to cover its surface to a depth of ¼ m to have dominated over the wind and to have retained its color. The actual minimum will be less by the factor by which the martian ionosphere deflects the solar wind. Hopefully martian orbiter measurements may provide this factor.

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### Irreversible Thermodynamics and Flow across Membranes

Bresler and Wendt (1) state that the solute permeability coefficient  $\omega$ —which appears in the formulation by Kedem and Katchalsky (2) of thermodynamic equations of flow across membranes—depends strongly on  $J_v$ , the volume flow, and therefore cannot be used to describe properties intrinsic to the membrane, “except for the case where  $J_v = 0$ , when  $\omega$  becomes constant.” However, when Bresler and Wendt’s Eq. 1 is linearized in  $J_v$ , the result is given by (3)

$$J_s = (D/RT\Delta x)\Delta\pi + \frac{1}{2}(C_s^A + C_s^B)J_v \quad (1)$$

where  $J_s$  is the total solute flow,  $D$  is the diffusion coefficient for the solute,  $R$  is the gas constant,  $T$  is the absolute

temperature,  $\Delta x$  is the thickness of the membrane, and  $C_s^A$  and  $C_s^B$  are the solute concentrations in compartments  $A$  and  $B$ , respectively. If the coefficient of  $\Delta\pi$  is identified with  $\omega$ , and that of  $J_v$  with  $\bar{C}_s$ , an average concentration, Eq. 1 is seen to be identical to Bresler and Wendt’s Eq. 2, which, in turn, is the result of the irreversible thermodynamic approach. Thus, the only limitation on the thermodynamic treatment is that it be restricted to sufficiently small forces and flows so that the relations between them are linear.

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2. O. Kedem and A. Katchalsky, *Biochim. Biophys. Acta* **27**, 229 (1958).
3. To obtain all the linear terms, it is necessary to expand the denominator in the right side of Bresler and Wendt’s Eq. 1 out to second-order terms.

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In developing his expansion of the Hertzian equation cited in our previous report (1), Manning does not, as he claims, arrive at the exact equation given by Kedem and Katchalsky (2) for solute flux. Instead he develops an equation to which theirs is an approximation, provided that a further rather severe restrictive assumption is made, namely,

$$C_s^A/C_s^B \approx 1$$

For a nonselective membrane ( $\sigma = 0$ ) (1), the following equations relate solute flow to volume flow. The Hertzian equation is given by

$$J_s = J_v \frac{C_s^B e^{-J_v \Delta\pi/D} - C_s^A}{e^{-J_v \Delta\pi/D} - 1} \quad (1)$$

Manning’s approximation of Eq. 1 is given by

$$J_s = J_v \frac{C_s^A + C_s^B}{2} + \omega \Delta\pi \quad (2)$$

Kedem and Katchalsky’s equation before approximations are made is as follows:

$$J_s = J_v \frac{C_s^A - C_s^B}{\ln C_s^A - \ln C_s^B} + \omega \Delta\pi \quad (3)$$

The limiting case for Eq. 1 at high volume flow is given by

$$J_s = J_v C_s^A \quad (4)$$

If we use a set of parameters for which  $\Delta C_s$  is small but  $C_s^A/C_s^B$  is significantly different from unity, we obtain the curves shown in Fig. 1. Inspection of Fig. 1 reveals, as expected,

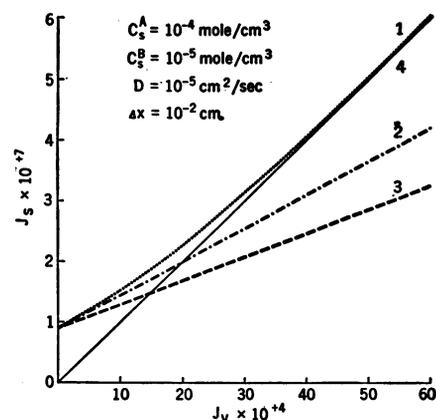


Fig. 1. Solute flow (in moles per square centimeter per second) as a function of volume flow (in milliliters per square centimeter per second) for Eqs. 1 through 4.

that at low values of  $J_v$ , Eq. 2 is a useful approximation to the exact result given by Eq. 1. At high values of  $J_v$ , Eq. 4 is the most useful. In no particular regime is Eq. 3 either exact or useful. Only if one makes two simultaneous, highly restrictive assumptions—that the flow is near zero and the concentration ratio is near unity (not concentration difference near zero)—does Eq. 3 become a reasonable approximation of Eq. 2, which in turn is an approximation of the exact result given by Eq. 1. In the thermodynamic derivation (2), Eq. 2 is regarded as an approximation of Eq. 3 which is in turn correctly regarded as giving the most exact result. We feel that these facts emphasize the unsuitability of the irreversible thermodynamic approach (which requires the application of Onsager’s reciprocity relation) for the system we describe. In contrast to irreversible processes such as combined diffusion and heat flow, the process we described has inherent mathematical nonlinearities which, without recourse to experiment, reveal that the system must be virtually at equilibrium before the flow equations are sufficiently linear so that Onsager’s reciprocity relations can be legitimately applied.

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## Irreversible Thermodynamics and Flow across Membranes

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