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DIFFUSION COEFFICIENTS IN HETEROGENEOUS MEDIA*

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April 4, 1972

ABSTRACT

In the general one-dimensional diffusion equation appear a diffusion coefficient, D , and an activity coefficient, γ . Under conditions of continuity, if γ depends only on concentration, then the steady-state distribution of concentration is a monotonic function of location. With such distributions conditions on D are derived for heretofore anomalous evaporation through membranes.

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The general equation for one-dimensional diffusion in a medium is (Jost, 1970, p. 156)

$$C_t = (C u \mu_x / N)_x \quad , \quad (1)$$

in which, and in what follows, subscripts denote partial derivatives, t and x are the time and space variables, respectively, N is Avogadro's number, and $C = C(x, t)$ is the molar concentration, $\mu = \mu(x, C)$ the chemical potential, and $u = u(x, C)$ the mobility of the diffusing substance. Relating the potential to concentration and activity coefficient, $\gamma = \gamma(x, C)$, allows writing eq. (1) as

$$C_t = [D(\gamma C)_x]_x \quad , \quad (2)$$

where the diffusion coefficient, $D = D(x, C)$, is proportional to u/γ and non-negative.

The steady-state form of eq. (2) is

$$D(\gamma C)_x = -P \quad (3)$$

for some constant, P . Eq. (3) shows that if D is continuous, then the steady-state activity, γC , is a monotonic function of x . This in turn implies that if $P \neq 0$ and γ is a function of C alone then a continuous steady-state C is itself a monotonic function of x . For otherwise C and hence γC would assume the same value at two distinct points in the medium, the monotonic γC would be constant between those points, and P would be zero.

More complicated steady-state distributions of concentration may be obtained, in particular, with the more general $\gamma = \gamma(x, C)$. Thus, for instance, if a steady-state concentration associated with diffusive flow through a continuous membrane should show a maximum within the membrane, then the activity coefficient would depend explicitly on location within the membrane.

When γ depends on x only through C , an assumption made tacitly by Jost (1960, p. 156) and others, then $(\gamma C)_x = (\gamma_C C + \gamma)C_x$, a form long recognized (Johnson, 1941; Birchenall and Mehl, 1947). Thus eq. (2) becomes

$$C_t = [D(\gamma_C C + \gamma)C_x]_x,$$

and with

$$D^* = D(\gamma_C C + \gamma) \tag{4}$$

eq. (2) assumes the more usual form of the diffusion equation,

$$C_t = (D^*C_x)_x \tag{5}$$

In this case the steady-state solution is monotonic as shown, and therefore the steady-state D^* cannot change sign.

Monotonic distributions of concentration suffice in principle for the description of certain membrane behavior, although explicit dependence of D on x may be necessary. For example, consider a membrane extending

in thickness from $x = 0$ to $x = 1$, and suppose the surface concentrations maintained at $C(0) = a$ and $C(1) = b$, $a \neq b$. With some biological or synthetic polymer membranes, interchanging a and b increases the steady-state flow through the membrane. Such membranes are called oriented. Suppose the flow, P , through an oriented membrane is given by the steady-state form of eq. (5): $-P = D^*C_x$. If D^* may be expressed as a product of two functions, each of a single variable: $D^*(x, C) = [1/f(x)] g(C)$, then

$$-P = \int_a^b g(C) dC \left[\int_0^1 f(x) dx \right]^{-1},$$

provided that both integrals exist. In this case, the interchange of a and b changes only the sign of P , reversing the flow but preserving its magnitude. Therefore, the diffusion coefficient of the oriented membrane cannot be separable in that way. In particular, D cannot be a function only of x or only of C . Crank (1956, p. 262) reached this conclusion in the same way.

Another example of the limitation of the diffusion coefficient is a problem in diffusion-controlled evaporation considered by Crank (1950; 1956, p. 289). Reported observations suggest that under certain conditions, the rate of evaporation of a substance through a membrane may be increased by increasing the concentration of the substance in the medium into which evaporation occurs. That is, evaporation into a humid atmosphere may be faster than into a dry atmosphere. These observations have until now defied explanation by ordinary diffusion methods. In the steady-state, the rate of evaporation is the flow through the membrane. Suppose this flow

given by $P = -D^*C_x$. As with oriented membranes, this D^* must depend explicitly on x and C and cannot be separable into appropriately integrable factors of a single variable each.

To fix ideas, let the membrane extend in thickness from $x = 0$ to $x = 1$, and denote by $C(x)$ or $C'(x)$ the distribution of concentration when the concentration at the evaporating surface is b or b' , respectively. Let $C(0) = C'(0) = 1$, and assume D^* continuous. The steady states are described by

$$D^*(x, C)C_x = -P \quad (7)$$

and

$$D^*(x, C')C'_x = -Q \quad (8)$$

where $Q > P$ for $b' > b$. Evaporation from the membrane surface at $x = 1$ implies $D^* \geq 0$. Eqs. (7) and (8) show that if, at some point x , $C'(x) = C(x)$ then $D^*[x, C(x)] = D^*[x, C'(x)] = 0$ or $C'_x(x) < C_x(x)$. If the latter held at every point of coincidence of C and C' , then $C'(x) \leq C(x)$ throughout the membrane and necessarily $b' \leq b$. Since $b' > b$ and $C'(0) = C(0)$, the steady-state D^* has a zero in the membrane. Moreover, if $D^*(0, 1) \neq 0$ then there is an $x' > 0$ where C and C' coincide and where $D^*(x', C) = 0$. Thus, it may be assumed that $D^*(0, 1) = 0$, for otherwise one deals with essentially the same evaporation problem in a membrane extending from $x = x'$ to $x = 1$, with $C(x') = C'(x')$ and $D^* = 0$ at the surface $x = x'$.

A D^* leading to the evaporative behavior described is

$$D^*(x, C) = 2x \sqrt{x} (1 - C)^{-2} .$$

Note that this D^* is not excluded by the foregoing since, although it is multiplicatively separable, the factors are not appropriately integrable.

Solving eq. (7) with this D^* and the boundary conditions $C(0) = 1$ and

$C(1) = 1 - a$ yields $C(x) = 1 - a \sqrt{x}$ and $P = 1/a$. For this solution, C ,

$D^*(x, C) = 2 \sqrt{x}/a^2$ and $D^*(0, 1) = 0$. Thus, as $C(1)$ increases, P

increases also.

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