Asymmetric diffusion in a nonlinear spatially inhomogeneous medium

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The nonlinear dependence of the impurity transport equations on concentration leads to different diffusion permeabilities in the forward and backward directions in an inhomogeneous solid layer. The asymmetry is calculated for using a two-layer membrane as an example.

Impurity particles often have an appreciable mobility and redistribute themselves by diffusion in an immobile solid carrier. High mobilities have been found for atomic hydrogen in metals,[1-3] for certain inert gases in glasses,[2,3] and for a number of molecular gases in zeolite crystals,[1,2] whose lattices have a characteristic porous structure. A plane layer of such a material is permeable to impurity molecules, and a constant difference in the conditions at its outer boundaries (e.g., a pressure drop of the permeating gas) creates a diffusion flux J.

The equations describing this process are nonlinear, since the diffusion coefficient $D(c)$ is in general a function of the impurity concentration c (as in the examples[2-4] we have mentioned) because of interactions between the impurity particles. Nonlinearity of the boundary conditions can be caused simply by saturation of the carrier by the permeating gas. Any kind of nonlinearity will cause the diffusion resistance of successive adjacent layers to become nonadditive and the permeability of a membrane whose structure is inhomogeneous over the thickness (i.e., when there is explicit dependence on the depth coordinate x in the transport equations) to become asymmetric: Transposing the external conditions changes not only the direction but also the magnitude of the flux. This is easy to understand qualitatively, but it would be of interest to make a quantitative estimate.

Suppose that the membrane consists of layers of different compositions A and B (with thicknesses a and b), in which the diffusion coefficients of gas C are D_A and D_B, and that the concentration of the gas on the outer sides of the membrane are c_A and c_B. For simplicity, we assume that molecules C on dissolving in the solid matrix occupy definite interstices, the number of which per unit volume (N_A and N_B) determines the solubility limit, and we let n be the concentration measured relative to the limiting concentration ($0\langle n < 1$). The flux from the gas phase into the solid is proportional to c_A and to the number of vacancies near the surface ($1 - n_A$), while the backward flux from the solid into the gas is proportional simply to n_A. The boundary condition arises because these microscopic fluxes are equal within a quantity of order J, which is a small quantity proportional to the ratio of the length of a diffusion jump to the macroscopic thickness of the layer. Making similar arguments for all the boundaries (CA, AB, BC) and denoting the solubility constants by K_A and K_B, we write the corresponding equations[1] for $x = -a$, $x = 0$, and $x = b$:

$$\frac{1}{c_A}\frac{n_A}{1-n_A}=K_A, \qquad \frac{n_{B0}(1-n_{A0})}{n_{A0}(1-n_{B0})}=K\equiv\frac{K_B}{K_A}$$

$$\frac{1}{c_B}\frac{n_B}{1-n_B}=K_B. \tag{1}$$

The steady-state flux is the same in any $x = $ const cross section of the membrane:

$$J=\frac{1}{a}D_A N_A(n_A-n_{A0})=\frac{1}{b}D_B N_B(n_{B0}-n_B). \tag{2}$$

Solving system (1), (2), we express the quantity of interest

$$J=j(N_A D_A N_B D_B/ab)^{1/2} \tag{3}$$

in terms of the smaller root j of the quadratic equation

$$j^2 F_2 - j F_1 + F_0 = 0,$$
$$F_0=k_A k_B(c_A-c_B), \quad F_2=(K_B-K_A)(1+K_A c_A)(1+K_B c_B),$$
$$F_1=(1+K_A c_A)(1+K_B c_B)\left(\lambda K_A+\frac{1}{\lambda}K_B\right)-(K_B-K_A)$$
$$\times\left[\left(\frac{1}{\lambda}-\lambda\right)K_A K_B c_A c_B+\frac{1}{\lambda}K_B c_B-\lambda K_A c_A\right], \tag{4}$$

where the dimensionless parameter λ characterizes the ratio of the layer thicknesses:

$$\lambda^2=N_A D_A b/N_B D_B a. \tag{5}$$

Equation (3)–(5) give the flux for any external conditions: at low pressures Eq. (1) can be linearized, so that the permeability is symmetric as long as the solubility obeys Henry's law; outside the region where Henry's law holds, for $c_{A(B)}K_B \gtrsim 1$, the value of J depends on the pressure, as is seen in Fig. 1. The asymmetry of the permeability is characterized by the ratio of the maximum values of the forward and backward fluxes:

$$A\equiv\frac{J_\to}{J_\gets}=\frac{[\Lambda^2+(K-1)]^{1/2}+\Lambda}{[\Lambda^2-(1-1/K)]^{1/2}+\Lambda}, \qquad \Lambda\equiv\frac{1}{2}\left(\lambda+\frac{1}{\lambda}\right). \tag{6}$$

It follows that the asymmetry is most pronounced for $\Lambda = \lambda = 1$, i.e., the layer thicknesses should be proportional to the corresponding diffusion coefficients, as can be seen from (5). Then for $K \gg 1$ the asymmetry coefficient can be estimated simply by direct inspection of the profile $n(x)$ shown in Fig. 2. The flux is proportional to the dropsin concentration, which for $\lambda = 1$ are the same across each of the layers and amount to $\Delta n \approx 1$ for the forward flux and $\Delta n \approx n_{A0} \approx 1 - n_{B0}\equiv\varepsilon\ll 1$ for the backward flux. The mid-
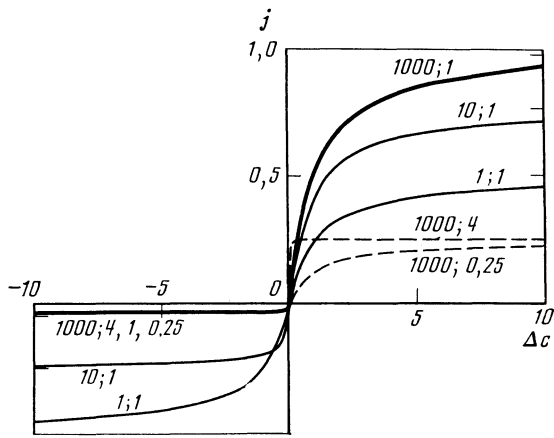
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FIG. 1. Reduced current j versus the concentration drop $\Delta c \equiv K_A (c_A - c_B)$ when the pressure on one side of the membrane is zero. The pairs of numbers $(K; \lambda)$ given on the curves are the equilibrium constant on the boundary between the layers and the ratio of the layer thicknesses. The curves corresponding to $K = 10^3$ are substantially asymmetric, and for $\Delta c < 0$ they run together.

dle boundary condition (1) gives the estimate $K\varepsilon^2 \sim 1$, so that the backward flux is smaller than the forward flux by a factor of $K^{1/2}$, and the coefficient $A \sim K^{1/2}$ is large, in agreement with (6).

The most suitable heterogeneous systems in which to observe the effect experimentally are those in which one of the layers is relatively inert with respect to the permeating gas (the heat of absorption Q is small), while the other has a large solubility constant. For example, large values $Q \gtrsim 10$ kcal/mole are typical for the absorption of a number of molecular gases (H_2O, NH_3, N_2, etc.) in zeolytes.[1,2] At temperatures somewhat above room temperature this corresponds to constants $K \gtrsim 10^6$, so that the forward and backward permeabilities can in principle differ by several orders of magnitude. In the diffusion of hydrogen through metallic bilayers (for example, Pd and Ni, which have a large sorption capacity and a low hydrogen solubility, respectively, or certain alloys[3-5]), the dissociative character of the dissolution will itself cause a nonlinearity of the bound-
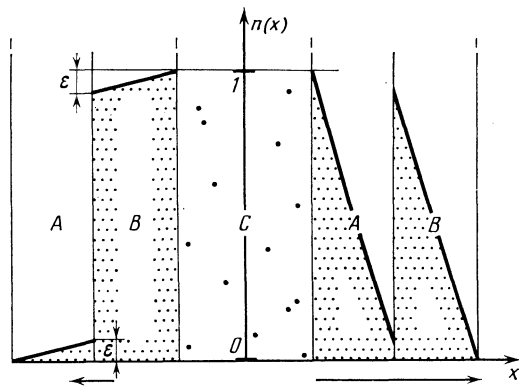

FIG. 2. Concentration distribution $n(x)$ at the limiting values of the forward and backward fluxes in the presence of well-defined nonuniformity, $K \gg 1$.

ary conditions ($n \propto c^{1/2}$), which can be taken into account straightforwardly in the calculation.

Finally, we note the interesting possibility that an analogous asymmetry of the heat conduction can arise because the thermal conductivity $\varkappa(T,x)$ depends simultaneously on the temperature and position although there is a fundamental difference from the diffusion case: an equilibrium jump of the temperature at the interfaces is impossible, unlike the analogous concentration jump in the problem treated.

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[1] The same result can be obtained by calculating the chemical potential $\mu(c,x)$ and requiring it to be continuous at the boundaries.

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[4] F. A. Lewis, J. P. Magennis, S. G. McKee, *et al.*, Nature **306**, 673 (1983).

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