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NOTE

On the State of a Binary Gas Mixture Near a Catalytic Surface

It is well known that the continuum equations of energy and momentum and their boundary conditions are strictly valid in the instance of a dilute gas only when the Knudsen number, l/a,* can be considered as zero.

For many systems involving gases at pressures of the order of atmospheric and higher, the Knudsen number is sufficiently small that the noncontinuum effects are unimportant. However, when one has, for example, a reaction occurring at the walls in the pores of a catalyst particle, or at the surface of a small particle, the Knudsen number can be large and the continuum considerations are no longer valid.

It is the purpose of this note to point out the deviation from continuum behavior found in a diffusing binary gas system near a catalytic surface. The particular physical system to be studied consists of an infinite plane catalytic surface at which the rearrangement reaction 1 → 2 is occurring. In the regimes specified by the Knudsen number, we shall, therefore, be considering only the limiting noncontinuum case where $l/a \rightarrow 0$.

Only the essentials of the derivation necessary for understanding the validity of the results will be sketched here.

We calculate the concentration distribution of molecules of type 1 and 2 near the surface from the single particle distribution function $f_i(\mathbf{r}, \mathbf{v})$ obtained by solution of the Boltzmann equation (1):

$$\mathbf{v}_i \cdot (\partial f_i/\partial \mathbf{r}) = \partial e f_i/\partial t \qquad i = 1,2 \qquad (1)$$

where $\partial e f_i/\partial t$ is the rate of change owing to encounters in the distribution function f_i at a fixed point in the system, $\mathbf{r}$; $\mathbf{v}_i$ is the velocity of a molecule of species i.

In the solution of Eq. (1) we consider only a small deviation $f_i^{(1)}$ from local thermodynamic equilibrium, $f_i^{(0)}$:

$$f_i = f_i^{(0)} + f_i^{(1)} \qquad i = 1,2 \qquad (2)$$

The effect of this assumption is that we are limited to a consideration of catalytic surface reactions of low efficiency. That is, the number of molecules of 2 created and 1 destroyed at the surface at a given time must be small relative to the total number of each species present at the surface.

Now $\partial e f_i/\partial t$ in Eq. (1) is a nonlinear term which we linearize in the following manner in order to obtain a solution of Eq. (1) in a useful form:

$$\mathbf{v}_i \cdot (\partial f_i/\partial \mathbf{r}) = \theta f_i^{(1)} \qquad i = 1,2 \qquad (3)$$

where θ can easily be shown to represent correctly the mutual diffusion of Maxwellian molecules, and:

$$\theta = \frac{1}{D_{12}}\left(\frac{kT}{m}\right) \qquad (4)$$

where D_{12} is the mutual diffusion coefficient, k, Boltzmann's constant; T, the temperature; and m the molecular mass. This Maxwellian model means that one is assuming only 1–2 collisions as giving rise to the mutual diffusion process.

The details of the deduction of the integral equations for f_i are analogous to the deduction of Welander (*2*) for the temperature-jump problem and will not be presented here.

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* l = molecular mean free path; a = a characteristic dimension of the physical system; for a cylindrical pore of a catalyst particle "a" would be the pore radius, or for a catalyst particle "a" would be the particle radius.

For the simple system of a rearrangement reaction and the collision model chosen, Eq. (3), the integral equations arising in the solution for f_i are not coupled and have the same form as the integral equation arising in the slip-velocity problem. The eigenvalue of the equation of the slip-velocity problem has been calculated from quadratures (*2*, *3*) and a numerical solution of the equation has been obtained (*3*).

Using the results of the slip-velocity problem, it may be shown that the concentration profile of species 2 for the present system has the form:

$$\frac{n_2(\xi) - n_2(0)}{(dn_1/d\xi)_\infty} = -\xi - [G_2(\xi) - G_2(0)] \qquad (5)$$

where ξ is a dimensionless distance:

$$\xi = \theta(m/2kT)^{1/2}x$$

and x is the perpendicular distance in the gas mixture from the catalytic surface which is taken at $x = 0$; $(dn_1/d\xi)_\infty$ represents the constant value of the concentration gradient of 1 found as $\xi \to \infty$. The function $G_2(\xi)$ may be represented by the approximate relation:

$$G_2(\xi) \approx 1.01[1.00 - 0.30(0.36\xi \ln \xi + 1.00)e^{-1.85\xi}] \qquad (6)$$

For the assumptions of this problem the total number density is constant, so that the profile for $n_1(\xi)$ is easily inferred. It may be seen that n_2 increases much more rapidly as one nears the wall than predicted by the corresponding linear continuum result. In a sense, the fraction of molecules leaving the wall relatively rich in 2 tends to "sweep" away the fraction of incoming molecules, relatively rich in 1.

If one assumes, as is customary in continuum calculations, that the concentration gradient is constant up to the surface, one has the obvious expression for the concentration profile:

$$\frac{n'_2(\xi) - n'_2(0)}{(dn_1/d\xi)_\infty} = -\xi \qquad (7)$$

here $n'_2(\xi)$ denotes the number density as determined from the erroneous assumption of a linear profile up to the surface.

Now at an infinite distance from the surface we require that $n'_2(\infty) = n_2(\infty)$. Therefore:

$$\lim_{\xi \to \infty} \left[\frac{n_2(0) - n'_2(0)}{(dn_1/d\xi)_\infty}\right] = [G_2(\infty) - G_2(0)] \qquad (8)$$

Rewriting this result in terms of species 1 we have from Eqs. (4) and (6):

$$n_1(0) - n'_1(0) = -\frac{D_{12}}{\frac{1}{2}(2kT/m)^{1/2}}[0.307](dn_1/dx)_\infty \qquad (9)$$

Introducing the mean free path, l, Eq. (9) becomes:

$$\Delta n_1(0) \equiv n_1(0) - n'_1(0) = -\alpha l[0.307](dn_1/dx)_\infty \qquad (10)$$

where $\alpha \approx 3/4$ is a constant.

Equation (10) has a purely formal similarity to the slip-velocity and temperature-jump expressions. Within the limits of the present analysis, indicated below, the magnitude of the error introduced by the erroneous assumption of linear concentration profiles in the present diffusion system may be seen from Eq. (10). It can be observed that the magnitude of the difference between the correct noncontinuum, $n_1(0)$, and incorrect continuum, $n'_1(0)$, surface concentrations for a fixed gradient is dependent only on the mean free path, l, and increases as the mean free path.

In the instance of a reaction occurring at the surface of a catalyst particle or pore, the foregoing considerations for an infinite plane wall may be taken to apply so long as one remains in what is termed the "slip-flow regime." The "slip-flow regime" has been found (*4*) to have the Knudsen number range $0 < l/a < 0.25$ where "a" denotes the radius of either the catalyst particle or pore. The extension of these results to $l/a > 0.25$ and to binary systems of unequal molecular masses would be of particular interest.

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