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A Kinetic Theory of Catalysis and Mass Transfer in a Cylinder

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The diffusion and mass transfer of a trace component in a background gas in a cylinder, is treated according to a relaxation transport equation. The system is assumed isothermal and at rest. An expression for an effective axial diffusivity is found which goes to the appropriate high and low density limits. Numerically, this diffusivity is similar to one half of the harmonic mean of the high density diffusivities, which is often used as an empirical extrapolating formula.

The radial mass transfer problem results in an integral equation which is solved numerically for all Knudsen numbers.

The case of catalytic reaction on the walls is considered in detail. Rarefaction effects become important under conditions of fast reaction. The problem of sublimation or evaporation from a cylinder wall can be treated by the same equations.

The effect of rarefaction (low density) on the utilization of an heterogeneous catalyst is of much interest in the field of chemical reaction engineering. In general, the techniques of Wheeler (*7*) as described in his pioneering paper do not seem to have been improved upon. An ad hoc approach is used in which a continuum formulation of the diffusion and reaction processes is made. To account for rarefaction, an empirical diffusivity is used which approaches the appropriate limit according to the value of the radial Knudsen number, N_{Kn} which is the ratio of the mean free path to some significant dimension.

The question of the appropriate diffusivity has been studied in some detail (*5*), and account has been taken of the complex geometric nature of the pore structure of a catalyst; but in most cases the diffusion has been considered separately from the reaction problem.

In recent years tremendous advances have been made in the kinetic theory of rarefied gases. However, only recently has the class of problems called "interior problems" been attacked successfully. The problem of the catalytic conversion of a trace dilute component gas in a cylinder is considered here from the viewpoint of the kinetic theory of gases. The geometry of the cylinder is used although the theory is readily applicable to any constant area, duct geometry.

It has been found that a class of mass transfer problems can be treated in this manner, and sublimation or evaporation is considered.

BACKGROUND

Hamel (*4*) has considered one dimensional mass transfer problems in perhaps the first rigorous treatment of Knudsen effects in a finite system. He included evaporation and catalysis as examples. Brock (*2*) has considered the Knudsen layer above a catalytic surface. This is the region roughly one mean path thick above a catalytic surface where the continuum theory has to break down. In general the effect of this region can be accounted for by slightly modifying the continuum boundary conditions. Hamel has also considered the Knudsen layer as a limiting case of his finite one dimensional problem.

FORMULATION OF THE PROBLEM

Consider a binary gas mixture. It is assumed that all properties of interest can be determined if the six dimensional distribution function f_1' can be determined. The Boltzmann equations for each of the species is

$$\frac{\partial f_1'}{\partial t} + \underline{v} \cdot \nabla f_1' = J_{12} + J_{11} \tag{1}$$

The left hand side of Equation (1) represents the convective contribution while the right hand side is the collisional contribution to the transport equation. The term, J_{12}, represents cross collisions, while J_{11} represents self collisions. The collision terms of Equation (1) are now approximated by a statistical model. The validity of this approximation is at least semiquantitative, judging from the results of recent papers on flow in interior geometries where theory and experiment have been compared, (3). These statistical models, sometimes called BGK type models, have one adjustable parameter, a relaxation time, τ which may be made a function of position or even of the velocity. This model may only be justified a posteriore, but at present is the only tractable method of treating this problem according to the kinetic theory of gases.

In general, if only diffusion is occurring, the relaxation time, τ can be chosen to fit a continuum Chapman-Enskog diffusivity. If only momentum transfer is occurring, τ can be chosen to yield the correct continuum viscosity. If several processes are occurring simultaneously, a single τ is not sufficient. The assumption that the species of interest is present in trace amounts is implicit, since the self collision term is omitted. Our steady state Boltzmann equation becomes

$$\underline{v} \cdot \nabla f' = \frac{f'_{LM} - f'}{\tau} \tag{2}$$

where

$$f'_{LM} = \left(\int f' d^3 v\right)\left(\frac{m}{2\pi kT}\right)^{3/2} \exp - \frac{m\, v^2}{2\, k\, T}$$

The subscript referring to species 1 with mass m, is omitted since we are concerned only with species 1. It is seen that Equation (2) is still an integrodifferential equation; but this is more amenable to analysis than the full Boltzman equation. The system is considered isothermal with negligible mass average velocity and τ' is considered constant. Hamel (4) discusses modeling of collision terms in general and the derivation of Equation (2) in particular.

It is now assumed that a reservoir of gas at equilibrium is adjacent to a single catalytic cylinder of radius R. The cylinder is presumed to be sufficiently long so that entrance effects are negligible. This restriction is made quantitative later. The exact nature of the flux boundary condition is left unspecified for the moment, but the distribution function at the wall contains a parameter K which allows the flux boundary conditions at the wall to be satisfied. The molecules which leave the wall are assumed to have a Maxwellian velocity distribution, that is the molecules are diffusely emitted from the wall. The boundary condition for the molecules leaving the wall are

$$f'(\underline{r}', z', \underline{v})_{r'=R} = Kn\, \rho(z') \left(\frac{m}{2\pi kT}\right)^{3/2} \exp - \frac{m\, v^2}{2\, k\, T} \qquad \underline{n} \cdot \underline{v} > 0 \tag{3}$$

Cylindrical coordinates are used with the z axis chosen to coincide with the axis of the cylinder. For $\underline{n} \cdot \underline{v} < 0$, the solution of Equation (2) is required.

The unit normal $\underline{n}$ is directed away from the wall. It is now convenient to make all quantities dimensionless. A unit velocity $v = (2\, k\, T/m)^{1/2}$, a unit density corresponding to the total density of the system (which is assumed constant) and a unit length corresponding to the radius of the cylinder R are chosen. The transport equation and boundary condition become

$$\underline{u} \cdot \nabla f = \frac{1}{\tau}\left[p \frac{e^{-u^2}}{\pi^{3/2}} - f \right] \tag{4}$$

where

$$p = \int f\, d^3 u$$

and

$$f(\underline{r}, z, \underline{u})\big|_{r=1} = \frac{K\rho(z)}{\pi^{3/2}}\, e^{-u^2} \qquad \underline{n} \cdot \underline{u} > 0$$

it is seen that

$$\tau = \tau' \left(\frac{2\, k\, T}{m}\right)^{1/2} /R$$

is equal to N_{Kn}.

SOLUTION OF THE PROBLEM

It is most convenient to perform all calculations with Cartesian coordinates so as not to introduce additional geometric terms in the Boltzmann equation.

It is assumed that

$$f = \rho(z) \left[\frac{e^{-u^2}}{\pi^{3/2}} - h(x, y, z, \underline{u}) \right] \tag{5}$$

Substituting this into Equation (4), neglecting $u_z \frac{\partial \rho}{\partial z} h$ and $u_z \rho \frac{\partial h}{\partial z}$, and assuming $\frac{\partial \ln \rho}{\partial z}$ is almost constant, the Boltzmann equation becomes

$$\tau \underline{c} \cdot \nabla_r h + h = g(\underline{r}) \frac{e^{-u^2}}{\pi^{3/2}} + \tau u_z \frac{d \ln \rho}{dz} \frac{e^{-u^2}}{\pi^{3/2}} \tag{6}$$

where

$$\underline{r} = (x, y), \quad \underline{c} = (u_x, u_y)$$

and

$$g(\underline{r}) = \int h\, d^3 u$$

These approximations are normally valid and are necessary in order to describe axial transfer by an axial diffusion type equation. The conditions when $\tau \left| \frac{d \ln \rho}{dz} \right| << 1$ are indicated explicitly since this condition is necessary for the approximations to be valid.

These are analogous approximations to the ones Cercignani and Sernagiotto (3) used in their solutions of the cylindrical Poiseuille flow problem with a BGK equation.

EFFECTIVE AXIAL DIFFUSIVITY

Let

$$F(\underline{r}, \underline{c}) = \int_{-\infty}^{\infty} u_z h \, d u_z \tag{7}$$

Multiplying Equation (6) by u_z and integrating over du_z it is found

$$\tau \underline{c} \cdot \nabla_r F + F = \frac{\tau}{2\pi} \frac{d \ln \rho}{dz} e^{-c^2} \tag{8}$$

This equation may be solved by integrating along the characteristics, namely

$$\tau c \frac{dF(\underline{r} + s \hat{c}, c)}{ds} + F = \frac{\tau}{2\pi} \frac{d \ln \rho}{dz} e^{-c^2} \tag{9}$$

with boundary condition $F(r, c)|_{r=1} = 0 \quad n \cdot c > 0$

This moment of h is zero because h is even in u_z, where

$$\hat{c} = \left(\frac{c_x}{|c|}, \frac{c_y}{|c|} \right)$$

Finally using the usual definition of diffusivity, the area averaged number flux is found to be (see Appendix)

$$R^2 \, \mathrm{v} \rho \int_A \int F \, d^2c \, d^2r = D_z \frac{d\rho}{dz} \frac{\pi R^2}{R} \tag{10}$$

where

$$D_z = \tau \, \mathrm{v} \, R \left[\frac{1}{2} - \frac{2}{\pi} \int_0^1 p \, dp \int_0^{\pi} d\alpha T_1 \left(\left| \sqrt{1 - p^2 \sin^2 \alpha} - p \cos \alpha \right| / \tau \right) \right]$$

in the diffusivity and

$$T_n(x) = \int_0^{\infty} y^n e^{-y^2 - x/y} \, dy$$

It is interesting to note that the continuum limit diffusivity, ($\tau \rightarrow 0$) corresponds to the diffusivity of a Chapman-Enskog solution to the transport Equation (2). The low density limit corresponds to Knudsen's result: $2/3 \, R v_{\text{thermal}}$.

The calculated diffusivity, D_z is plotted on Figure 1 along with two empirical diffusivities which share the same limiting values as D_z in the low and high density limit. The low density limit is, of course, independent of the collision term in the Boltzmann equation.

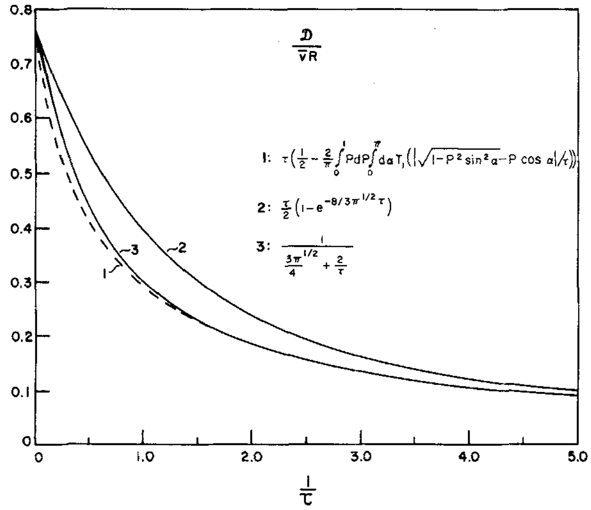

Fig. 1. Dimensionless diffusivity vs. inverse Knudsen number. Curve 1 is from the text, curve 2 is due to Wheeler (7) and curve 3 is suggested by Pollard and Present (6).

RADIAL CONCENTRATION PROFILE

Let

$$\Gamma(\underline{r}, \underline{c}) = \int_{-\infty}^{\infty} h(\underline{r}, \underline{u}) \, du_z \tag{11}$$

By integrating Equation (6) over all u_z, the following equation results

$$\tau \underline{c} \, \nabla_r \Gamma + \Gamma = g(\underline{r}) \frac{e^{-c^2}}{\pi} \tag{12}$$

with boundary condition

$$\Gamma(\underline{r}, \underline{c})|_{r=1} = (1 - K) \frac{e^{-c^2}}{\pi} \quad \underline{n} \cdot \underline{c} > 0$$

By integrating along the characteristics, it is found that

$$\Gamma(r, c) = (1 - K) \frac{e^{-\frac{b}{\tau c} - c^2}}{\pi} + \frac{1}{\pi \tau} \int_0^b \frac{e^{-\frac{s}{\tau c} - c^2}}{c} g(\underline{r} - s \hat{c}) \, ds \tag{13}$$

The quantity b is the length of the characteristic from the boundary of the cylinder through (x, y) with direction $\hat{c} = \left(\frac{c_x}{c}, \frac{c_y}{c} \right)$.

Noting that $\int \Gamma d^2c = g$, Equation (13) may be transformed into the integral equation

$$\tilde{g}(\underline{r}) = \frac{1}{\pi} \int e^{-\frac{b}{\tau c} - c^2} d^2c + \frac{1}{\pi \tau} \int_A \frac{dX dY \, \tilde{g}(X, Y) T_0 \left(\sqrt{(X - x)^2 + (Y - y)^2} / \tau \right)}{\sqrt{(X - x)^2 + (Y - y)^2}} \tag{14}$$

where $\tilde{g}(\underline{r}) = g(\underline{r}) / (1 - K)$.

This Fredholm integral equation is similar to the one encountered by Cercignani and Sernagiotto (3) in their solution of cylindrical Poiseuille flow, differing only in the inhomogeneous term. It is noted that Equation (14) for $\tilde{g}(\underline{r})$ is independent of the flux boundary conditions incorporated in K. Hamel (4) also found that the finite one dimensional problem integral equation is independent of the flux boundary condition.

There are two fairly straightforward modes of solution which are efficient for all τ, both due to Cercignani and Sernagiotto. The first involves numerical solution directly from the integral equation by means of appropriate finite differencing. The second involves constructing a variational principal. It appears however that the variational principal is not, in general, an absolute minimum (or maximum) principal but only an extremum. In particular the difference in value between the functional with the correct function and the functional with the trial function is only one signed for the class of positive trial functions, which is rather restrictive, linear combinations of trial functions are not necessarily positive. On account of these considerations it was decided to employ the former method. The mode of finite differencing that was used, was identical to the one of Cercignani and Sernagiotto and involved a special form of differencing to eliminate the singularity in the kernel of

Equation (14) and a change of the variables of integration after differencing.

The final form of the set of equations is

$$\sum_{k=1}^{N} (\alpha_{hk} + \delta_{hk})\, \tilde{g}_k = a_h; \quad h = 1, \ldots\ldots, N$$

where

$$\tilde{g}_k = \tilde{g}(r_k - \Delta/2)$$

$$r_k = k\Delta; \quad \Delta = 1/N$$

$$a_h = \frac{2}{\pi}\int_o^{\pi} T_1[|(r_h - \Delta/2) \cos\psi$$
$$+ \sqrt{1 - (r_h - \Delta/2)^2 \sin^2\psi}|/\tau]\psi$$

$$\alpha_{hk} = -\frac{2}{\pi}\Big(\int_o^{\pi} d\psi\ T_1(|(r_h - \Delta/2) \cos\psi$$
$$+ \sqrt{(r_k - \Delta)^2 - (r_h - \Delta/2)^2 \sin^2\psi}|/\tau)$$
$$- \int_o^{\pi} d\psi\ T_1\, [|(r_h - \Delta/2) \cos\psi$$
$$+ \sqrt{r_k{}^2 - (r_h - \Delta/2)^2 \sin^2\psi}|/\tau), \quad k > h,$$

$$\frac{2}{\pi}\int_o^{\pi} d\psi\ T_1(|(r_h - \Delta/2)\cos\psi$$
$$+ \sqrt{r_k{}^2 - (r_h - \Delta/2)\ \sin^2\psi}|/\tau)$$
$$-\frac{2}{\pi}\int_o^{\arcsin[(r_h-\Delta/2)/(r_k-\Delta)]} d\psi\, [T_1(|\ r_h - \Delta/2)\cos\psi$$
$$+ \sqrt{(r_k - \Delta)^2 - (r_h - \Delta/2)^2 \sin^2\psi}|/\tau)$$
$$- T_1\,(|(r_h - \Delta/2)\cos\psi$$
$$- \sqrt{(r_k - \Delta)^2 - (r_h - \Delta/2)^2 \sin^2\psi}|/\tau)\,], \quad k = h,$$

$$-\frac{2}{\pi}\int_o^{\arcsin[(r_k-\Delta)/(r_h-\Delta/2)]} [T_1\,(|(r_h - \Delta/2)\cos\psi$$
$$+ \sqrt{(r_k - \Delta)^2 - (r_h - \Delta/2)^2 \sin^2\psi}|/\tau)$$
$$- T_1\,(|(r_h - \Delta/2)\cos\psi$$
$$- \sqrt{(r_k - \Delta)^2 - (r_h - \Delta/2)^2 \sin^2\psi}|/\tau)\,]$$
$$+\frac{2}{\pi}\int_o^{\arcsin[r_k/(r_h-\Delta/2)]} d\psi\, [T_1\,(|(r_h - \Delta/2)\cos\psi$$
$$+ \sqrt{r_k{}^2 - (r_h - \Delta/2)^2 \sin^2\psi}|/\tau)$$
$$- T_1\,(|(r_h - \Delta/2)\cos\psi$$
$$- \sqrt{r_k{}^2 - (r_h - \Delta/2)^2 \sin^2\psi}|/\tau)\,] \quad k < h \qquad (15)$$

A quantity of interest that is calculated once $\tilde{g}(r)$ is known is the flux in the radial direction:

$$-j_r/(1 - K)\rho\ n\,\mathrm{v} = \frac{x}{r}\int c_x\Gamma\ d^2c + \frac{y}{r}\int c_y\Gamma\ d^2c \qquad (16)$$

Since j_r is axially symmetric and we are interested only in $r = 1$, the following expression for the flux to the wall is obtained:

$$j_r/(1 - K)\ \rho\ n\,\mathrm{v}_{r=1} = \Lambda(\tau)$$
$$= -\frac{2}{\pi}\int_o^{\pi/2} d\psi \cos\psi\, T_2\,(2\cos\psi/\tau) - \frac{2}{\pi}\int_o^{\pi} d\psi \cos\psi\, T_2(0)$$
$$-\frac{1}{\pi\tau}\int_o^{1} W\,dW\,\tilde{g}(W)$$
$$\int_0^{2\pi} \frac{d\psi\, T_1((1 + W^2 - 2W\cos\psi)^{1/2}/\tau)\,(1 - W\cos\psi)}{(1 + W^2 - 2\,W\cos\psi)} \qquad (17)$$

This may readily be evaluated by approximating the integral containing $\tilde{g}(r)$ of Equation (17) by a sum similar to one used to solve Equation (14), which is designed to eliminate the singularity and then change the variables of integration and hence perform one of the integrations analytically. Angular integrations have to be performed numerically and a ten point Gaussian integration was found to be adequate. The transcendental functions $T_1(x)$ and $T_2(x)$ were evaluated to four significant figures using a power series for small x and an asymptotic series for large x, both of which were obtained from Abramowitz and Stegun (*1*).

The dimensionless concentration profile of the perturbation, $\tilde{g}$ is plotted on Figure 2, the dimensionless flux on Figure 3, and the area averaged perturbation on Figure 4. It is noted that the concentration field is given by $\rho(z)[1 - (1 - K)\,\tilde{g}(r)]$.

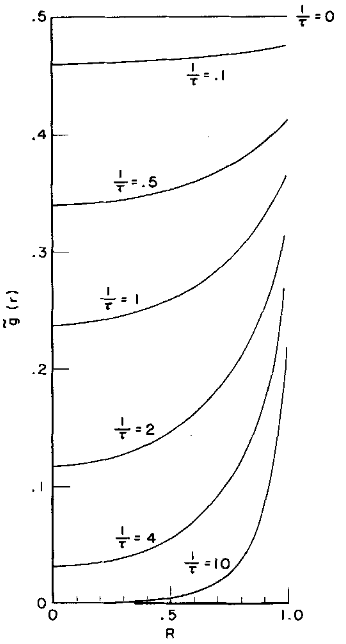

Fig. 2. Dimensionless concentration perturbation profile at various Knudsen numbers.

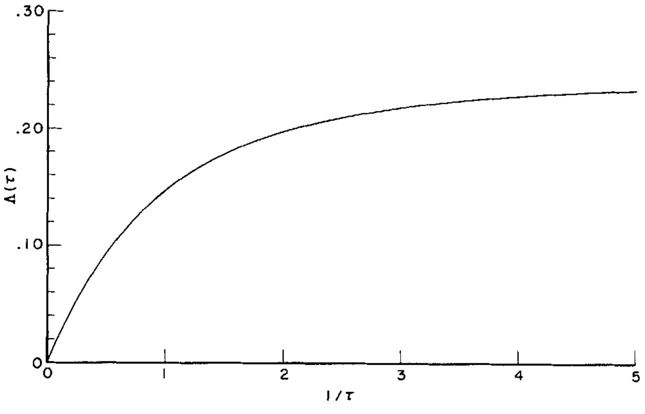

Fig. 3. The dimensionless radial flux, $\Lambda(\tau)$ at the wall vs. inverse Knudsen number.

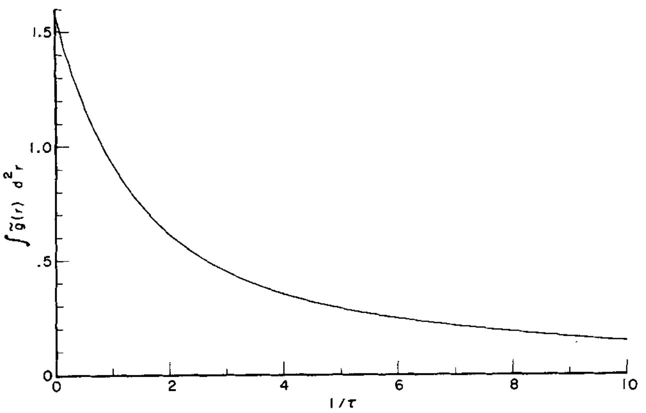

Fig. 4. Area averaged perturbation, $\int \tilde{g}\, d^2r$ vs. inverse Knudsen number.

CATALYTIC REACTION ON THE CYLINDER WALL

The simplest description of the catalytic process involves a chemical accommodation coefficient. This parameter, γ, is assumed to be independent of surface coverage, although this restriction can be removed under suitable conditions. The flux boundary condition for the radial flux j_r, and the emitted radial flux $\bar{j}_r$ is now given by

$$j_r|_{r=1} = -\gamma/(1-\gamma) j_r|_{r=1} \qquad (18a)$$

and thus

$$K = \frac{\Lambda}{\Lambda + \gamma/(1-\gamma)\, 2\pi^{1/2}} \qquad (18b)$$

Equation (18*b*) is obtained by substituting Equation (17) into Equation (18*a*) and using the boundary condition in Equation (3).

Just as in a Chapman-Enskog solution of a transport equation, it is necessary to use the continuity equation to obtain the concentration field of $\rho(z)$. Consider a number balance on a slice of the cylinder normal to the axial direction. The equation describing $\rho(z)$ is

$$\pi R^2 D_z \frac{d^2\rho}{d(zR)^2} - (2\pi R) K \rho \mathrm{v} \frac{\gamma}{2\pi^{1/2}(1-\gamma)} = 0 \qquad (19)$$

This implies that by using Equation (18)

$$\frac{d \ln \rho}{dz} = -a \tanh [a(L-z)] \qquad (20)$$

where

$$a = \left[\frac{2\mathrm{v}R}{D_z} \left(\frac{1}{1/\Lambda + (1-\gamma)\, 2\pi^{1/2}/\gamma} \right) \right]^{1/2}$$

It is perhaps useful to consider the axial concentration gradient as being composed of two resistances, one due to rarefaction effects and one due to chemical reaction effects. This is similar to Hamel's results for the one dimensional problem. This is in addition to an effective axial diffusivity. A conventional ad hoc approach with an empirical diffusivity is valid when the term $1/(\Lambda)$ is negligible compared to $(1-\gamma)2\pi^{1/2}/\gamma$. The efficiency, ϵ, of the catalytic pore is defined as the net number of molecules going into the pore per total number going in.

The net number of molecules is given by Equation (10). The total number of molecules going down the cylinder is now determined. Multiplying Equation (6) by u_z and integrating over positive u_z, the following equation results:

$$\tau c \cdot \nabla_r H + H = g(r) \frac{e^{-c^2}}{2\pi^{3/2}} + \frac{\tau}{4\pi} \frac{d \ln \rho}{dz} e^{-c^2} \qquad (21)$$

where

$$H = \int_0^\infty u_z h \, d u_z$$

and the boundary condition becomes

$$H(\underline{r}, \underline{c})|_{r=1} = \frac{(1-K)e^{-c^2}}{2\pi^{3/2}} \quad n \cdot c > 0 \qquad (21a)$$

The solution to Equation (21) is found by integrating along the characteristics. After some algebraic manipulation, the following expression for the velocity average of the quantity H results.

$$\int H\, d^2c = \frac{(1-K)}{2\pi^{3/2}} \int e^{-b/\tau c - c^2}\, d^2c \qquad (22)$$

$$+ \frac{1}{2\pi^{3/2}\tau}$$

$$\int_A \frac{dX\, dY\, g(X,Y)\, T_o\left(\sqrt{(X-x)^2 + Y - y)^2}/\tau\right) \cdot}{\sqrt{(X-x)^2 + (Y-y)^2}}$$

$$+ \frac{1}{4\pi} \frac{d \ln \rho}{dz} \int d^2c \int_o^b \frac{e^{-c^2 - s/\tau c}\, ds}{c} \qquad (22a)$$

where the quantity b is defined under Equation (13). Substituting from Equation (14) and integrating over the cross section of the cylinder

$$\int_A d^2r \int d^2c\, H = \frac{(1-K)}{2\pi^{1/2}} \int_A \tilde{g}(r)\, d^2r + \frac{1}{2} \int d^2c \int_A d^2r\, F \qquad (23)$$

where F is the function defined by Equation (7).

Finally the following expression for the efficiency results.

$$\epsilon = \frac{\pi R^2 D_z\, d\rho/d(zR)}{\rho \mathrm{v} R\left[-\pi^{1/2}/2 + \frac{(1-K)}{2\pi^{1/2}} \int_A \tilde{g}(r)\, d^2r + \frac{\pi}{2} \frac{D_z}{\mathrm{v}R} d\rho/d(zR) \right]} \qquad (24)$$

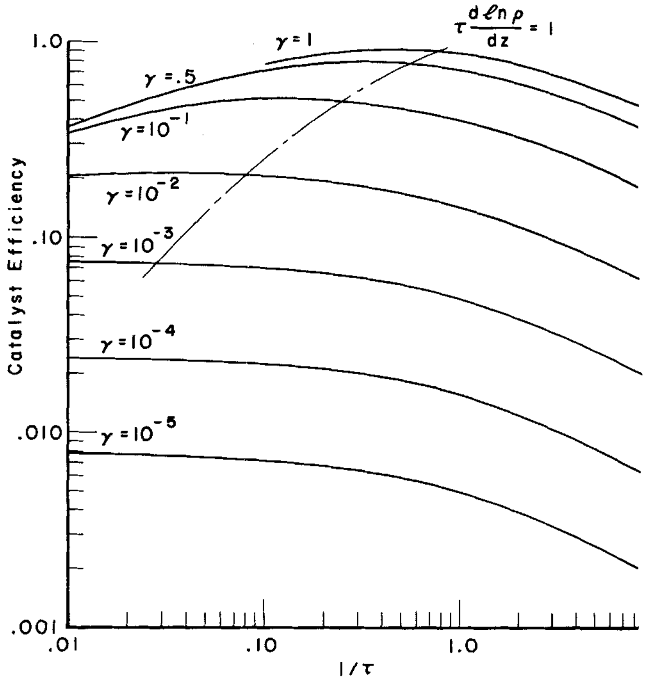

Fig. 5. Catalyst efficiency against log of the inverse Knudsen number for various chemical accommodation coefficients.

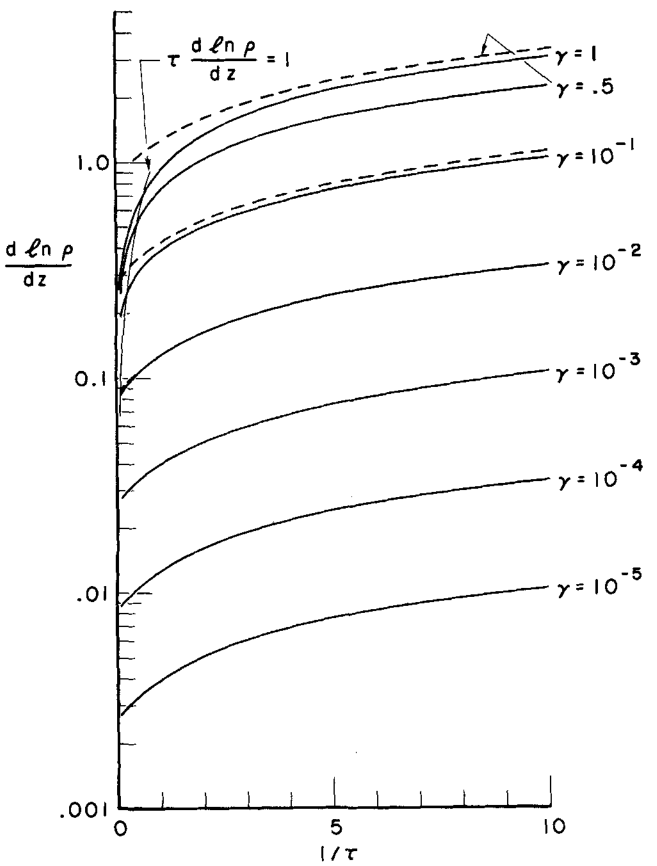

Fig. 6. Dimensionless axial concentration gradient vs. inverse Knudsen number for various chemical accommodation coefficients.

The efficiency of the pore and $d \ln \rho/(dz)$ are plotted on Figures 5 and 6 respectively for the case of an effectively infinite pore. The effect of a finite length is to lower the efficiency of the pore; but at low enough Knudsen number, the efficiency has to approach the efficiency of the infinite pore. It should be noted that this theory is only valid when τ/L and $\tau d \ln\rho/(dz)$ are small. The line $\tau d \ln\rho/(dz) = 1$ is drawn on Figures 5 and 6 to indicate the approximate region of validity of the calculation. On Figure 6, the dashed lines indicate $d \ln\rho/(dz)$ without the contribution from $1/\Lambda$, the rarefaction resistance. It is observed that this approximation is valid providing γ is small, that is for slow reaction rates. The maximum in efficiency appears to coincide with the region where the solution becomes invalid.

SUBLIMATION OR EVAPORATION FROM THE WALLS OF A CYLINDER

The theory is also valid for the case of sublimation or evaporation from the walls of a cylinder, where the concentration at the entrance of the cylinder is maintained at a concentration different from the equilibrium vapor pressure of the evaporating medium.

The boundary condition at $r = 1$ is obtained by setting the net flux to the wall equal to the condensation rate less the evaporation rate from the volatile surface:

$$j_r\big|_{r=1} = \alpha j_r^+\big|_{r=1} - \frac{\alpha \rho_{\text{eq}}\, \mathrm{v}n}{2\pi^{1/2}} \tag{25}$$

The sticking coefficient α is assumed equal to the evaporation coefficient, and ρ_{eq} is the mole fraction corresponding to the equilibrium vapor pressure of the volatile medium at the total density of interest.

The following expression results for K and the net flux to the wall,

$$j_r\big|_{r=1} = \frac{(\rho - \rho_{\text{eq}})\mathrm{v}n}{1/\Lambda + 2\pi^{1/2}(1-\alpha)/\alpha} \tag{26}$$

$$K = \frac{\Lambda\rho + \alpha\rho_{\text{eq}}/(1-\alpha)2\pi^{1/2}}{\Lambda\rho + \alpha\rho/(1-\alpha)2\pi^{1/2}} \tag{26a}$$

From a balance over a slice of the cylinder, the following equation is obtained for the concentration field of $\rho(z)$:

$$\frac{d^2\rho}{dz^2} - \frac{2\mathrm{v}R(\rho - \rho_{\text{eq}})}{D_z[1/\Lambda + 2\pi^{1/2}(1-\alpha)/\alpha]} = 0 \tag{27}$$

The similarity between Equation (27) and (19) is apparent. The radial flux has a resistance due to rarefaction and to the kinetics of evaporation. The expression for the dimensionless slope is

$$\frac{d \ln(\rho - \rho_{\text{eq}})}{dz} = -a \tanh\left(a(L-z)\right) \tag{28}$$

where

$$a = \left[\frac{2\mathrm{v}R}{D_z}\left(\frac{1}{1/\Lambda + (1-\alpha)2\pi^{1/2}/\alpha}\right)\right]^{1/2}$$

The expression for the efficiency of the pore for sublimation or evaporation is identical with Equation (24) with K given by Equation (26a). The expression for ϵ in this case is

$$\epsilon = \frac{\pi D_z/\mathrm{v}R \qquad d\ln(\rho - \rho_{\text{eq}})/dz}{\frac{-\pi^{1/2}}{2}\rho/(\rho - \rho_{\text{eq}}) + \int_A \frac{\tilde{g}\, d^2r}{(1-\alpha)2\pi^{1/2}/\alpha + \Lambda} + \frac{\pi}{2}\frac{D_z}{\mathrm{v}R}\frac{d\ln(\rho - \rho_{\text{eq}})}{dz}} \tag{29}$$

where $d \ln(\rho - \rho_{\text{eq}})/dz$ is given by Equation (28). When $\rho_{\text{eq}} << \rho$, the efficiency is identical with that for catalysis of the walls.

The coefficient α is observed to be very close to one, and the curve corresponding to $\gamma = 1$ on Figure 5 is appropriate for sublimation.

CONCLUSIONS

The BGK transport equation is solved for the case of a trace component in a cylindrical geometry under isothermal, zero mass flow conditions. Reaction or sublimation is allowed to occur on the wall. Under conditions where both the axial Knudsen number and the average axial concentration gradient are small, the molecular flux in the axial direction is described by a Fickian type equation with an effective diffusivity. This diffusivity goes to the Chapman-Enskog diffusivity at high density and to the usual Knudsen diffusivity at low density.

The radial problem was found to be solvable, independent of the particular processes occurring on the wall. An integral equation which describes the perturbation of the concentration field was solved over the whole range of radial Knudsen number.

The results were specialized to catalysis and sublimation. In both cases it was found that the flux to the wall of the cylinder was composed of a resistance to the kinetic effects and a resistance due to rarefaction effects. For catalysis, the rarefaction other than an appropriate axial diffusivity are important only for high reaction rates. In sublimation rarefaction effects are usually limiting.

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NOTATION

a = dimensionless concentration gradient
$\underline{c}$ = (u_x, u_y) dimensionless velocity
$\hat{c}$ = $\underline{c}/|\underline{c}|$
D_z = effective axial diffusivity
$F(\underline{r}, \underline{c}) = \int_{-\infty}^{\infty} u_z\, h\, d\, u_z$
f' = six dimensional distribution function
f = $f'/n\mathrm{v}^3$, dimensionless distribution function
g = $\int h\, d^3\, u$
$\tilde{g}$ = $g/(1-K)$
H = $\int_0^{\infty} v_z\, h\, d\, v_z$
h = perturbation to local Maxwellian distribution function
J_{ij} = collision term in Boltzmann equation between species i, j
j_r^- = radial number flux
j_r = radial number flux leaving wall
K = parameter determined by flux boundary condition
k = Boltzmann's constant
L = length, in radii
m = mass of molecule of interest
N_{Kn} = $\tau'\mathrm{v}/R$, Knudsen number
n = total number density
$\underline{n}$ = unit vector normal to cylinder wall
R = radius of cylinder
$\underline{r}$ = $(x, y) = \underline{r'}/R$
$\underline{r'}$ = (x', y')
T = temperature
$T_n(x) = \int_0^{\infty} y^n \exp\,[-y^2 - x/y]\, d\, y$
$\underline{u}$ = $(u_x, u_y, u_z) = \underline{v}/\overline{v}$, components of dimensionless velocity
v = (v_x, v_y, v_z) molecular velocity
v = $(2\, kT/m)^{1/2}$, reference velocity
v_{therm} = $(8\, kT/\pi m)^{1/2}$, average thermal speed at equilibrium
X, Y = dummy variables
$(x, y, z) = (x', y', z')/R$, dimensionless coordinates
(x', y', z') = coordinates with z' axis coinciding with axis of cylinder

Greek Letters

α = probability of evaporation or condensation
γ = chemical accommodation coefficient, probability of reaction
Γ = $\int_{-\infty}^{\infty} h\, du_z$
δ_{hk} = Kronecker delta function
Δ = finite difference dimensionless length increment
ϵ = efficiency of cylinder for either reaction or sublimation
Λ = dimensionless radial flux
ψ = dummy angle variable
ρ = mole fraction of local Maxwellian
ρ_{eq} = saturation mole fraction
τ = dimensionless relaxation time = N_{Kn}
τ' = molecular relaxation time
∇' = $\left(\frac{\partial}{\partial x'}, \frac{\partial}{\partial y'}, \frac{\partial}{\partial z'}\right)$
∇_r = $\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}\right)$
∇ = $\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$
$\int_A d^2r$ = integration over cross section area of cylinder

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APPENDIX

Calculation of Effective Axial Diffusivity

The solution of Equation (9) is

$$F(\underline{r}, \underline{c}) = \frac{1}{2\pi}\frac{d\ln\rho}{dz}\int_0^b \frac{e^{-c^2-s/\tau c}}{c}\, ds \qquad (1A)$$

where b is defined under Equation. (13).

Integrate F over all of the velocity space using cylindrical coordinates and transform variables of integration $d\,\theta\, ds$ to $dXdY$ where $X = x - s\cos\theta$ and $Y = y - s\sin\theta$. The following expression for the local dimensionless flux results

$$-\int F\, d^2\, c = -\frac{1}{2\pi}\frac{d\ln\rho}{dz}$$

$$\int_A \frac{dXdY\;\; T_o\left(\sqrt{(X-x)^2 + (Y-y)^2}/\tau\right)}{\sqrt{(X-x)^2 + (Y-y)^2}} \qquad (2A)$$

The effective axial diffusivity is now obtained by integrating the local flux over the area of the cylinder:

$$\frac{D_z(\tau)}{\mathrm{v}R} = \frac{1}{2\pi^2}$$

$$\int_A dXdY \int_A dxdy\, \frac{T_o\left(\sqrt{(X-x)^2 + (Y-y)^2/\tau}\right)}{\sqrt{(X-x)^2 + (Y-y)^2}} \qquad (3A)$$

Twofold of this fourfold integration can be performed analytically. The coordinates are shifted to coincide with (X, Y) and new variables of integration$(X-x,\ Y-y)$ are introduced in polar coordinates. This is the transformation used by Cercignani and Sernagiotto (3), and results in D_z given under Equation (10). The final integrations must be evaluated numerically in a manner similar to Equation (15). Special care must be taken because the integral is discontinuous in the transformed variables.