EXPERIMENTAL DETERMINATION OF MUTUAL-DIFFUSION COEFFICIENTS IN GASES

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A steady-state solution is found for the distributions of concentration, pressure, and mass-average velocity along a capillary joining two gas-filled volumes with and without an account of diffusive "slip." Despite the mass-average motion, experimental data can be analyzed on the basis of the ordinary Fick's law. The experimental results are compared with equations for the mutual-diffusion coefficient given by the rigorous Chapman–Enskog kinetic theory.

INTRODUCTION

Diffusive transport in the ordinary type of diffusion apparatus (consisting of two volumes containing different gases and connected by a capillary) is determined from a simple expression for the flux density of one of the components. This expression is based on the assumption of a constant pressure in the volumes and in the capillary, but the expression given for the diffusive flux density by the rigorous kinetic theory of gases shows that this assumption is not valid. If the masses of the diffusing molecules are significantly different, the pressure cannot be constant along the capillary, so a mass-average velocity arises in the capillary and considerably complicates the transport.

We are therefore faced with the question of the extent to which the diffusion coefficients found experimentally in this type of apparatus can be compared with the theoretical Chapman–Enskog equations, found in the coordinate system moving with the mass-average velocity.

§ 1. Analysis Neglecting Diffusive Slip

The state of the gas at any point in the capillary at any time is described by the closed system of

\[
\begin{align*}
1) & \quad \frac{\partial n}{\partial t} + \text{div} n \mathbf{v} = 0, \\
2) & \quad \frac{\partial n}{\partial t} + \text{div} n \mathbf{v} = 0, \\
3) & \quad \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = -\frac{1}{\rho} \nabla p + \frac{\gamma}{\rho} \Delta \mathbf{v}.
\end{align*}
\]

In the steady-state one-dimensional case we have

\[
\begin{align*}
1) & \quad \rho \mathbf{v} = A, \\
2) & \quad n \mathbf{v} = B, \\
3) & \quad v \frac{\partial \mathbf{v}}{\partial x} = -\frac{1}{\rho} \frac{\partial \rho}{\partial x} + \frac{\gamma}{\rho} \left( \frac{\partial^2 \mathbf{v}}{\partial x^2} + \frac{\partial^2 \mathbf{v}}{\partial y^2} \right).
\end{align*}
\]

In Eqs. (1) and (2), \( \omega \) is the number-average velocity [1],

\[
\omega = v + \frac{1}{n} (I_1/m_1 + I_2/m_2), \quad I_1 = -\frac{n^2}{\rho} m_1 m_2 D \frac{\partial \mathbf{c}}{\partial x}, \quad I_1 + I_2 \equiv 0, \quad c = n_i/n.
\]

From the first two equations in system (2) we find

\[
\begin{align*}
1) & \quad v n Y = A, \\
2) & \quad v n + \frac{m_2 - m_1}{m_1 m_2} I_1 = B, \\
Y & = c m_1 + (1 - c) m_2.
\end{align*}
\]
The solution of this system is

\[ Y = F \exp \left[ Bx/nD \right] + \frac{A}{B}. \]  

(4)

Setting \( Y = Y_0 \) at \( x = 0 \) and \( Y = Y_L \) at \( x = L \), we find the integration constant \( F \) and the ratio \( A/B \):

\[ Y = Y_0 \exp \left[ Bx/nD \right] \left( 1 - \exp \left[ Bx/nD \right] \right). \]  

(5)

\[ \frac{A}{B} = \frac{Y_L - Y_0 \exp \left[ BL/nD \right]}{1 - \exp \left[ BL/nD \right]}. \]

To find \( B \) we must turn to equation of motion (3) for system (2). Analysis of the terms in this equation shows that it simplifies considerably when

\[ \frac{r^2}{L^2} \ll 1, \quad \frac{r^2}{L^2} \ll 1. \]  

(6)

In Eqs. (6), \( r \) is the capillary radius, \( L \) is the capillary length, and \( \bar{Y} \) is a certain average mass of the mixture "molecule."

When conditions (6) hold, we find from the equation of motion the Poiseuille equation

\[ v = -\frac{r^2}{8\eta} \frac{d\rho}{dx}. \]  

(7)

In Eq. (7), \( v \) is the mass-average velocity averaged over the capillary cross section, and \( \eta \) is a certain average viscosity of the mixture.

Combining Eq. (7) with Eq. (1) from system (3), we find the distribution of the total density of molecules along the capillary:

\[ n^2 = \frac{2B}{r^2} x \frac{2nD}{a} \ln Y + F; \quad a = -kT \frac{r^2}{8\eta}. \]  

(8)

If we have \( n = n_0 \) at \( x = 0 \) and \( n = n_L \) at \( x = L \), then, taking \( F \) and \( B \) from (8), we find

\[ n^2 = n_0^2 + \frac{2B}{a} x \frac{2nD}{a} \ln \frac{Y_L}{Y_0}; \quad B = -\frac{a}{2L} (n_L^2 - n_0^2) + \frac{nD}{L} \ln \frac{Y_L}{Y_0}. \]  

(9)

We turn now to the two particular cases of \( B = 0 \) and \( n_0 = n_L \). With \( B = 0 \), we see easily from (5) that the concentration in the capillary changes linearly:

\[ Y = Y_0 + (Y_L - Y_0) \frac{x}{L}; \quad c = c_0 + (c_L - c_0) \frac{x}{L}. \]  

(10)

It also follows from (9) that

\[ \Delta p = p_0 - p_L = -\frac{8Dn}{r^2} \ln \frac{Y_L}{Y_0}. \]  

(11)

Equation (11) is the familiar expression for the baroeffect during the mutual diffusion of gases in a capillary [2]. From Eqs. (5) and (3) we find expressions for \( A \) and \( v \):

\[ A = (Y_o - Y_L) \frac{nD}{L}; \quad v = \frac{A}{nY}. \]  

(12)

If \( c_0 = 1 \) and \( c_L = 0 \), the average-mass velocities at the ends of the capillary are

\[ v_0 = \frac{m_1 - m_2}{m_1} \frac{D}{L}; \quad v_L = \frac{m_1 - m_2}{m_2} \frac{D}{L}. \]  

(13)

The number density for the flux of the first component is

\[ G_i = \nu_i \frac{f}{m_1} = nD \frac{c_o - c_L}{L} = -nD \frac{\partial c}{\partial x}. \]  

(14)