THERMAL DIFFUSION FACTOR IN GAS MIXTURES-DUFOUR EFFECT (I)

A. Boushehri
Department of Chemistry, University of Shiraz, Shiraz, Iran.

A. Maghari*
Department of Chemistry, University of Tehran, Tehran, Iran.

(Received 20th Nov. 1989)
(Approved 26th Nov. 1990)

ABSTRACT

The thermal diffusion factor, $a_T$, for a binary gas mixture is calculated on the basis of nonequilibrium thermodynamics. A new formula for $a_T$ is derived and this factor is given for several pairs of gases according to this formula.

INTRODUCTION

The term Dufour effect refers to the creation of a transient temperature gradient as a result of an initial concentration gradient during interdiffusion of gases. This effect was discovered by Dufour[1] in 1872, but not investigated until its rediscovery by Clusius and Waldmann[2] in 1942. This phenomenon is a result of energy transport accompanying the process of diffusion in gases. It is, therefore, associated with the existence of a concentration gradient and may be regarded as the inverse of the thermal diffusion (Soret effect) in which a temperature gradient causes a concentration gradient. Diffusion thermo-effect (Dufour effect) can yield information about the thermal diffusion factor and can be used as a supplement to "thermal diffusion" measurements.

In view of the local approximation, the entropy production and flux density vector are given by:

$$\sigma = \sum_{ab} X_a X_b$$

(sum convention)

$$\mathbf{J} = \sum_{\mu} \mathbf{X}_\mu$$

(1)

(2)

where the symbol $\mu$ denotes the complete

*Corresponding author
contraction of the tensors; \( \gamma \) and \( \gamma' \) denote the vector and tensor representations, respectively. In these equations \( X \)'s and \( L \)'s are the forces and phenomenological coefficients, respectively.

For an isotropic medium, the vector processes in which the mass diffusion and energy transfer both occur:

\[
\sigma = \gamma^H \frac{\partial}{\partial T} \gamma^H \frac{\partial}{\partial T} \left( \frac{\partial}{\partial T} \frac{\partial \mu_i}{\partial T} \right)
\]

where \( \gamma^H \) and \( \gamma^H \) are the flux density vectors for energy and mass, respectively; \( \mu_i \) is the chemical potential of component \( i \), and \( T \) is the absolute temperature. In two components gaseous system, if one designates \( \frac{\partial \mu_i}{\partial T} = f(T, P, \xi_1) \), then at constant pressure

\[
\gamma^H \frac{\partial}{\partial T} \gamma^H = \left( \frac{I}{T^2} \right) \gamma^H + (1/T)(\partial \mu_1/\partial \xi_1)_{T,P} \times \gamma_1
\]

where \( H_i \) is the enthalpy of component \( i \), and \( \xi_1 \) is the mass fraction of component 1. Using the Gibbs-Duhem relation, for a perfect gas mixture, it can easily be shown:

\[
\sigma = -(1/T^2) \gamma^H \gamma^H - (1/T^2) \left( \frac{\partial \mu_1}{\partial \xi_1} \right)_{T,P} \gamma_1
\]

with:

\[
\gamma^H = \gamma^H - \gamma^H \gamma^H
\]

The comparison of eq. (5) with eq. (1) and Eq. (2) gives:

\[
\gamma^H = -(1/T^2) \gamma^H
\]

\[
\gamma_1 = -(1/T^2) \left( \frac{\partial \mu_1}{\partial \xi_1} \right)_{T,P} \gamma_1
\]

On the other hand, thermal conductivity, diffusivity and thermal diffusion factor are defined, respectively:

\[
\lambda = \frac{L_{qq}}{T^2}
\]

\[
D_{12} = \left( \frac{L_{11}}{\rho \xi_2 T} \right) \left( \frac{\partial \mu_1}{\partial \xi_1} \right)_{T,P}
\]

\[
\alpha = \left( \frac{L_{1q}}{L_{11} \xi_1} \right) \left( \frac{\partial \mu_1}{\partial \xi_1} \right)^{-1}
\]

where \( \rho \) is the total mass density. Using the Onsager's reciprocity law \( (L_{1q} = L_{1q}) \) and substituting eq. (7) into eq. (2), one obtains:

\[
\frac{\partial \xi}{\partial T} = -\lambda \frac{\partial T}{\partial T} \frac{\partial \mu_1}{\partial \xi_1} - \xi_1 \frac{\partial q}{\partial T} D_{12} \alpha \frac{\partial \xi_1}{\partial T}
\]

for heat conduction.

The energy conservation equation in local form is:

\[
\frac{\partial H}{\partial T} \frac{\partial T}{\partial T} = -\gamma^H \gamma^H
\]

where \( H(r) \) is the classical Hamiltonian of the system (energy per mass).

In the absence of convection, eq. (13) reduces to:

\[
\rho C_p \left( \frac{\partial T}{\partial t} \right) = -\gamma^H \gamma^H
\]

where \( C_p \) is heat capacity of the mixture. Substituting eq. (12) into eq. (14), it is found that:

\[
\lambda \gamma^H \frac{\partial T}{\partial T} + \xi_1 \frac{\partial \mu_1}{\partial \xi_1} - \frac{\partial q}{\partial T} D_{12} \alpha \frac{\partial \xi_1}{\partial T}
\]

At the maximum temperature, the left hand side of this equation is zero, hence:

\[
\lambda \gamma^H \frac{\partial T}{\partial T} + \xi_1 \frac{\partial \mu_1}{\partial \xi_1} - \frac{\partial q}{\partial T} D_{12} \alpha \frac{\partial \xi_1}{\partial T} = \kappa(t)
\]

where \( \kappa(t) \) is a function of time only, and of course independent of coordinates.

Using eq. (16), Rastogi and Madan [3] have calculated \( \alpha \), supposing \( \kappa \) is zero; while Boushehri and Afrashtehfar
[4] have considered as a constant being dependent to the geometry of the diffusion apparatus.

In this article, we are interested in exact calculation of the thermal diffusion factor, $\alpha_T$, according to eq. (15). The values obtained for some pairs of gases are compared with those found on the basis of the kinetic theory of gases.

**Theoretical Calculation of $\alpha_T$**

Consider the infinite system sketched below. Suppose two pure gases (labeled with subscripts 1 and 2), initially at the same temperature and pressure placed in the regions 1 and 2, respectively.

The temperature is monitored at points $x_1$ and $x_2$ symmetrically placed about the origin (intersection of gases). That is, $x_1 = -L/2$ and $x_2 = L/2$.

\[ \frac{\partial T}{\partial t} = \eta \frac{d^2 T}{dx^2} + \xi \frac{d^2 \zeta_1}{dx^2} \]  

(17)

where:

\[ \zeta = \left( \frac{\rho_1}{\rho C_p} \right) \left( \frac{\partial \mu_1}{\partial \zeta_1} \right) T_0, P_0, D_{12} \alpha_T \]  

(18-a)

\[ \eta = \lambda / \rho C_p \]  

(18-b)

eq. (15) can be written in one dimensional form as:

To and $P_0$ are temperature and pressure, respectively.

Boundary conditions of eq. (17) are:

\[ T(-\infty, t) = T(\infty, t) = T(x, 0) = 0 \]

Following deGroot and Mazur's [5] treatment in considering the diffusion equation one may neglect the thermal diffusion; therefore:

\[ \frac{\partial \zeta_1}{\partial t} = D_{12} \frac{\partial^2 \zeta_1}{\partial x^2} \]

(19)

with boundary conditions:

\[ \zeta_1(\infty, t) = 0, \zeta_1(-\infty, t) = 1 \]  

and

\[ \zeta_1(x, 0) = \Theta(x) \]

where $\Theta(x)$ is the Heaviside unit step function defined as:

\[ \Theta(x) = \begin{cases} 1 & x < 0 \\ 0 & x > 0 \end{cases} \]

$\delta(x')$ is Dirac delta function.

The appropriate solution of eq. (19) is:

\[ \zeta_1(x, t) = \frac{1}{2} \text{Erfc} \left[ \frac{x}{2(D_{12} t)^{1/4}} \right] \]

(20)

where Erfc is complementary error function. We may write eq. (17) as:

\[ \frac{\partial T}{\partial t} = \eta \frac{d^2 T}{dx^2} + \gamma(t) \chi(x, t) \]

(21)

where:

\[ \gamma(t) = \left[ 4D_{12} t (\pi D_{12} t)^{1/4} \right]^{-1} \]

(22-a)

\[ \chi(x, t) = \xi x \exp \left( -x^2 / 4D_{12} t \right) \]

(22-b)

By using the Fourier transformation technique, eq. (21) transforms to:

\[ \partial T(w, t) / \partial t + \eta w^2 T(w, t) = \gamma(t) \chi(w, t) \]

(23)
and the solution of this equation is:

\[ T(w,t) = \int_0^t \exp\left[ -\eta w^2 (t-t') \right] \chi(t') dt' \]

\[ \chi(w,t') = (2\pi)^{-\frac{1}{2}} \int_{-\infty}^{\infty} dx \ e^{iwx} \chi(x,t) \]

and:

\[ T(x,t) = (2\pi)^{-\frac{1}{2}} \int_{-\infty}^{\infty} dw \ e^{-iwx} T(w,t) \]

The appropriate solution of eq. (25) is:

\[ \chi(w,t') = \frac{i\xi(2D_{12}t')^{3/2}}{w} \exp\left( -D_{12}t'w^2 \right) \]

(27)

Inserting eq. (27) into eq. (24) and substituting into eq. (26), and integrating it over the \( w \) and \( t' \), the final result is:

\[ T(x,t) = \frac{\xi(\eta-D_{12})^{-1}}{2}\left\{ \text{Erf}[x/2(D_{12}t)^{1/2}] - \text{Erf}[x/2(\eta t)^{1/2}] \right\} \]

(28)

The measured temperature difference is defined as:

\[ \delta T = T(x_2,t) - T(x_1,t) \]

(29)

If eq. (28) is substituted into eq. (29), the maximum temperature difference, \( \delta T_{\text{max}} \), would be found as:

\[ \delta T_{\text{max}} = \frac{2\eta \ln(\eta/D_{12})}{2D_{12}\ln(\eta/D_{12})} \frac{\xi}{\eta-D_{12}} \left( \text{Erf}\left[ \frac{x}{2(D_{12}t)^{1/2}} \right] - \text{Erf}\left[ \frac{x}{2(\eta t)^{1/2}} \right] \right) \]

(30)

Values of \( \delta T_{\text{max}} \) can be determined experimentally.

Putting eq. (18-a) into eq. (30), the thermal diffusion factor, \( \alpha_T \), is obtained:

\[ \alpha_T = \frac{\rho(\eta-D_{12})C_p \delta T_{\text{max}}}{D_{12}\rho_1(\partial \mu_1/\partial \xi_1)T_0D_0} \Omega \]

where:

\[ \Omega = \frac{2\eta \ln(\eta/D_{12})}{\eta-D_{12}} \]

(31)

(32)

Thus, estimation of the thermal diffusion factor, through eq. (31), is a rather easy task.

RESULTS AND DISCUSSION

If we assume that the gas mixture is perfect, then eq. (31) can be written as:

\[ \alpha_T = \frac{(\eta-D_{12})C_p \delta T_{\text{max}}}{D_{12}RT_0} \left[ \frac{\xi}{M_2^2-M_1^2} + M_1 \right] \]

(33)

where \( M_1 \) and \( M_2 \) are the molar masses.

Eq. (33), along with experimental \( \delta T_{\text{max}} \) values, allow the estimation of the thermal diffusion factors. The results of such calculations for some gas pairs are given in Table 1. The values of the thermal diffusion factors obtained directly from thermal diffusion measurements are also shown for comparison purposes. The lack of close agreement between the theoretical and experimental values in some cases may be due to the use of pure component values of \( \lambda, \rho_1 \) and \( C_p \) in eq. (33), as well as the imperfect nature of the gases which has not been considered.
Table 1: Comparison between theoretical and experimental values of thermal diffusion factors for some gas pair mixtures

<table>
<thead>
<tr>
<th>System</th>
<th>$\delta T_{max}$</th>
<th>$\alpha_T$ from $\text{eq. (33)}$</th>
<th>$\alpha_T$ from thermal diffusion measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2/\text{H}_2$</td>
<td>0.18$^a$</td>
<td>0.38</td>
<td>0.34(288-373)$^b$</td>
</tr>
<tr>
<td>He/A</td>
<td>0.26$^a$</td>
<td>0.33</td>
<td>0.37(288-373)$^b$</td>
</tr>
<tr>
<td>$\text{CH}_4/\text{H}_2$</td>
<td>0.13$^a$</td>
<td>0.19</td>
<td>0.22(190-300)$^b$</td>
</tr>
<tr>
<td>He/CO$_2$</td>
<td>0.30$^a$</td>
<td>0.44</td>
<td>0.44(366)$^c$</td>
</tr>
</tbody>
</table>

a: The values of $\delta T_{max}$ measured at 25°C and 700 torr reported by Ref[6].
b: Ref[7]
c: Ref[8]

REFERENCES