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

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ABSTRACT

The thermal diffusion factor,α_T,for a binary gas mixture is calculated on the basis of nonequilibrium thermodynamics. A new formula for α_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 thermoeffect(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 approxima - tion,the entropy production and flux density vector are given by:

$$\sigma = L_{\alpha\beta} : X_\beta \; X_\alpha \qquad \text{(sum convention)}$$

$$(1)$$

$$\underset{\sim}{J} = \underset{\sim}{L} \; \underset{\sim}{X}$$

$$(2)$$

where the symbol:denotes the complete

contraction of the tensors; $\sim$ and $\underset{\sim}{\sim}$ denote the vector and tensor repre - sentations,respectively. In these equations X's and L's are the forces and phenomenological coefficients,res- pectively.

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

$$\sigma = \underset{\sim}{J}_H \cdot \underset{\sim}{\nabla}(1/T) - \Sigma_i \underset{\sim}{J}_i \cdot \underset{\sim}{\nabla}(\mu_i/T) \tag{3}$$

where $\underset{\sim}{J}_H$ and $\underset{\sim}{J}_i$ are the flux density vectors for energy and mass,respec - tively; μ_i is the chemical potential of component i,and T is the obsolute temperature. In two components gase- ous system,if one designates $(\mu_i/T) = f(T,P,\zeta_1)$,then at constant pressure

$$\underset{\sim}{\nabla}(\mu_i/T) = -(H_i/T^2)\underset{\sim}{\nabla}T + (1/T)(\partial\mu_1/\partial\zeta_1)_{T,p}$$
$$x \ \underset{\sim}{\nabla}\zeta_1 \tag{4}$$

where H_i is the enthalpy of component i,and ζ_1 is the mass fraction of com- ponent 1. Using the Gibbs-Duhem rela- tion,for a perfect gas mixture,it can easily be shown:

$$\sigma = -(1/T^2)\underset{\sim}{J}_q \cdot \underset{\sim}{\nabla}T - (1/\zeta_2 T)(\partial\mu_1/\partial\zeta_1)_{T,p}$$
$$\underset{\sim}{J}_1 \cdot \underset{\sim}{\nabla}\zeta_1 \tag{5}$$

with: $\underset{\sim}{J}_q = \underset{\sim}{J}_H - \Sigma H_i \underset{\sim}{J}_i \tag{6}$

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

$$\underset{\sim}{X}_q = -(1/T^2)\underset{\sim}{\nabla}T \tag{7}$$

$$\underset{\sim}{X}_1 = -(1/\zeta_2 T)(\partial\mu_1/\partial\zeta_1)_{T,p}\underset{\sim}{\nabla}\zeta_1 \tag{8}$$

On the other hand,thermal conduc- tivity,diffusivity and thermal dif - fusion factor are defined,respectively:

$$\lambda = L_{qq}/T^2 \tag{9}$$

$$D_{12} = (L_{11}/\rho\zeta_2 T)(\partial\mu_1/\partial\zeta_1)_{T,p} \tag{10}$$

$$\alpha_T = (L_{1q}/L_{11}\zeta_1)(\partial\mu_1/\partial\zeta_1)^{-1}_{T,p} \tag{11}$$

where ρ is the total mass density. Using the Onsager's reciprocity law $(L_{1q}=L_{q1})$ and substituting eq.(7)-(11) into eq.(2),one obtains:

$$\underset{\sim}{J}_q = -\lambda\underset{\sim}{\nabla}T - \rho_1(\partial\mu_1/\partial\zeta_1)_{T,p} D_{12}\alpha_T\underset{\sim}{\nabla}\zeta_1 \tag{12}$$

for heat conduction.

The energy conservation equation in local form is:

$$\frac{\partial\rho H(\underset{\sim}{r})}{\partial t} = -\underset{\sim}{\nabla}\cdot\underset{\sim}{J}(\underset{\sim}{r}) \tag{13}$$

where $H(\underset{\sim}{r})$ is the classical Hamilto- nian of the system(energy per mass). In the absence of convection,eq.(13) reduces to:

$$\rho C_p(\partial T/\partial t) = -\underset{\sim}{\nabla}\cdot\underset{\sim}{J}_q \tag{14}$$

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

$$\rho C_p(\partial T/\partial t) = \underset{\sim}{\nabla}\cdot\{\lambda\underset{\sim}{\nabla}T + \rho_1(\partial\mu_1/\partial\zeta_1)_{T,p} D_{12}\alpha_T\underset{\sim}{\nabla}\zeta_1\} \tag{15}$$

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

$$\lambda\underset{\sim}{\nabla}T_{max} + \rho_1(\partial\mu_1/\partial\zeta_1)_{T,p}D_{12}\alpha_T\underset{\sim}{\nabla}\zeta_1 = \underset{\sim}{K}(t) \tag{16}$$

where $\underset{\sim}{K}(t)$ is a function of time only, and of course independent of coordi- nates.

Using eq.(16),Rastogi and Madan [3]have calculated α_T,supposing $\underset{\sim}{K}$ 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,α_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 α_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 $X_2=L/2$.
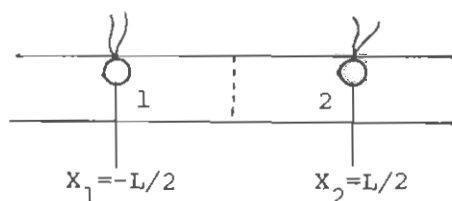
$$\partial T/\partial t=\eta d^2 T/dx^2 + \xi d^2\zeta_1/dx^2 \qquad (17)$$

where:

$$\xi=(\rho_1/\rho C_p)(\partial\mu_1/\partial\zeta_1)_{T_0,P_0} D_{12}\ \alpha_T \qquad (18\text{-}a)$$

$$\eta=\lambda/\rho C_p \qquad (18\text{-}b)$$

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

To and p_0 are temperature and pres - sure,respectively.

Boundary conditions of eq.(17) are :

$$T(-\infty,t)=T(\infty,t)=T(x,o)=0$$

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

$$\partial\zeta_1/\partial t=D_{12}(\partial^2\zeta_1/\partial x^2) \qquad (19)$$

with boundary conditions:

$$\zeta_1(\infty,t)=o,\zeta_1(-\infty,t)=1 \qquad \text{and}$$
$$\zeta_1(x,o)=\Theta(x)$$

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

$$\Theta(x)=\int_x^\infty dx'\ \delta(x')= \begin{cases} 1 & x < 0 \\ 0 & x > 0 \end{cases}$$

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

The appropriate solution of eq.(19)is:

$$\zeta_1(x,t)=\tfrac{1}{2}\ \text{Erfc}[x/2(D_{12}t)^{\frac{1}{2}}] \qquad (20)$$

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

$$\partial T/\partial t=\eta(d^2 T/dx^2)+\gamma(t)\ \chi(x,t) \qquad (21)$$

where:

$$\gamma(t)=[4D_{12}t(\pi D_{12}t)^{\frac{1}{2}}]^{-1} \qquad (22\text{-}a)$$

$$\chi(x,t)=\xi x\ \exp(-x^2/4D_{12}t) \qquad (22\text{-}b)$$

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

$$dT(w,t)/dt +\eta w^2 T(w,t)=\gamma(t)\ \chi(w,t) \qquad (23)$$

and the solution of this equation is:

$$T(w,t)=\int_0^t \exp[-\eta w^2(t-t')]\gamma(t')\,\chi(w,t')dt' \tag{24}$$

where:

$$\chi(w,t')=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{\infty} dx\, e^{iwx}\,\chi(x,t) \tag{25}$$

and:

$$T(x,t)=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{\infty} dw\, e^{-iwx}\,T(w,t) \tag{26}$$

The appropriate solution of eq.(25) is:

$$\chi(w,t')=i\xi(2D_{12}t')^{3/2}w\,\exp(-D_{12}t'w^2) \tag{27}$$

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

$$T(x,t)=\frac{1}{2}\xi(\eta-D_{12})^{-1}\{Erf[x/2(D_{12}t)^{\frac{1}{2}}]-Erf[x/2(\eta t)^{\frac{1}{2}}]\} \tag{28}$$

The measured temperature difference is defined as:

$$\delta T=T(x_2,t)-T(x_1,t) \tag{29}$$

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

$$\delta T_{max}=\frac{1}{2}\xi(\eta-D_{12})^{-1}\{Erf^{\frac{1}{2}}[\frac{2\eta\ln(\eta/D_{12})}{\eta-D_{12}}]^{\frac{1}{2}}-Erf^{\frac{1}{2}}[\frac{2D_{12}\ln(\eta/D_{12})}{\eta-D_{12}}]^{\frac{1}{2}}\} \tag{30}$$

Values of δT_{max} can be determined experimentally.

Putting eq.(18-a) into eq.(30), the

thermal diffusion factor, α_T, is obtained:

$$\alpha_T=\frac{\rho(\eta-D_{12})C_p\,\delta T_{max}}{D_{12}\rho_1(\partial\mu_1/\partial\zeta_1)_{T_0,P_0}}\Omega \tag{31}$$

where:

$$\Omega=\{Erf^{\frac{1}{2}}[\frac{2\eta\ln(\eta/D_{12})}{\eta-D_{12}}]^{\frac{1}{2}}-Erf^{\frac{1}{2}}[\frac{2D_{12}\ln(\eta/D_{12})}{\eta-D_{12}}]^{\frac{1}{2}}\}^{-1} \tag{32}$$

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

RESULTS AND DISCUSSION

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

$$\alpha_T=\frac{(\eta-D_{12})C_p\,\delta T_{max}}{D_{12}RT_0}[\zeta_1(M_2-M_1)+M_1]\Omega \tag{33}$$

where M_1 and M_2 are the molar masses. Eq.(33), along with experimental δT_{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 λ, ρ_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 experi-

mental values of thermal diffusion factors

for some gas pair mixtures

System	δT_{max}	α_T, from eq.(33)	α_T, from thermal diffusion mea - surements
N_2/H_2	0.18^a	0.38	$0.34(288-373)^b$
He/A	0.26^a	0.33	$0.37(288-373)^b$
CH_4/H_2	0.13^a	0.19	$0.22(190-300)^b$
He/CO_2	0.30^a	0.44	$0.44(366)^c$

a:The values of δT_{max} measured at $25\,^\circ C$ and 700

torr reported by Ref[6].

b:Ref[7]

c:Ref[8]

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