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Dufour Effect in Gases

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A study of the Dufour effect was made for five different gas mixtures: H_2–N_2, H_2–O_2, H_2–N_2O, He–N_2O and He–O_2. Measurements were made at 25 °C under 700 Torr. The values of the thermal diffusion factor were calculated for the above mixtures from the experimental data on the basis of the thermodynamics of irreversible processes.

The diffusion thermoeffect is perhaps the least investigated of the transport properties of gases. It involves the measurement of the transient temperature gradient which results from an initial concentration gradient as interdiffusion takes place. It is, of course, closely related to the inverse phenomenon of thermal diffusion. In this work five different gas mixtures are investigated. No previous measurements of the diffusion thermoeffect are known to have been made for H_2–N_2O, He–N_2O, and He–O_2 mixtures.

The effect was originally discovered by Dufour[1] in 1872, but not understood, until after its rediscovery by Clusius and Waldmann[2] in 1942. Rastogi and Madan[3] have recently studied the Dufour effect using a two-bulb interdiffusion apparatus with appropriately located thermocouples similar to the one used in the present work. Sawford *et al.*[4] and Mason *et al.*[5] have studied several aspects of the phenomenon in gases. A study of the temperature dependence of the diffusion thermoeffect was made by Boushehri.[6]

The Chapman-Enskog kinetic theory of this effect is well-known,[7,8] and provides a means of obtaining the thermal diffusion factor (α) from observations of the temperature difference as a function of time. The thermal diffusion factor was obtained very conveniently from the observation of the maximum temperature only. This maximum temperature difference occurs shortly after interdiffusion of the gases begins and there is thus no need to determine the temperature difference as a function of time which would be necessary if the Chapman-Enskog kinetic theory were used to calculate the thermal diffusion factor.

Theoretical Consideration

Our starting point is the well-known equation for the entropy production per unit volume (σ) in a motionless fluid of uniform density in which diffusion of matter and transfer of energy both occur[9]:

$$\sigma = J_{\mathrm{u},\mathrm{x}}\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{1}{T}\right) - \sum_i J_{i,\mathrm{x}}\frac{\mathrm{d}}{\mathrm{d}x}(\mu_i/T) \qquad (1)$$

where $J_{\mathrm{u},\mathrm{x}}$ and $J_{i,\mathrm{x}}$ are the energy flux density and mass flux density of component i in the x-direction (the "flux density" is defined as the amount of energy or mass crossing unit area perpendicular to the direction of flow—the x-axis-per unit of time); μ_i is the chemical potential per unit mass, and T is the absolute temperature. Equation (1) expresses the general idea that rate of production of entropy can be written as the algebraic sum of the product of "fluxes" and "forces" ($\sigma = J_k X_k$, where J_k has the form of a flux density and X_k—the thermodyanamic "force" has the general nature of a gradient).

It is convenient to write the entropy production in a different form. To do this, we begin with the relation:

$$\mathrm{d}(\mu_i/T)/\mathrm{d}x = (1/T)(\mathrm{d}\mu_i/\mathrm{d}x)_T - (H_i/T^2)(\mathrm{d}T/\mathrm{d}x)$$

where the specific enthalpy of component i is given by the Gibbs-Helmholtz equation:

$$H_i = -T^2[\partial(\mu_i/T)/\partial T]_p$$

We also introduce a new flux defined by

$$J_\mathrm{q} = J_{\mathrm{u},\mathrm{x}} - \sum H_i J_{i,\mathrm{x}},$$

and Eq. (1) may then be written in the form:

$$\sigma = -\frac{J_\mathrm{q}}{T^2}\frac{\mathrm{d}T}{\mathrm{d}x} - \sum\frac{J_i\mathrm{d}\mu_i}{T\mathrm{d}x} \qquad (2)$$

where J_i is an abbreviation for $J_{i,\mathrm{x}}$. For a two-component system (i=1,2), Eq. (2) becomes

$$\sigma = -\frac{J_\mathrm{q}}{T^2}\frac{\mathrm{d}T}{\mathrm{d}x} - \frac{J_1}{T}\frac{\mathrm{d}\mu_1}{\mathrm{d}x} - \frac{J_2}{T}\frac{\mathrm{d}\mu_2}{\mathrm{d}x} \qquad (3)$$

In this system, the two flows are not independent, since $J_1+J_2=0$. If we now use the Gibbs-Duhem equation,

$$C_1(\mathrm{d}\mu_1/\mathrm{d}x) + C_2(\mathrm{d}\mu_2/\mathrm{d}x) = 0$$

at constant temperature and pressure, Eq. (3) may be written as

$$\sigma = -\frac{J_\mathrm{q}}{T^2}\frac{\mathrm{d}T}{\mathrm{d}x} - \frac{J_1}{C_2T}\left(\frac{\partial\mu_1}{\partial C_1}\right)_{T,p}\frac{\mathrm{d}C_1}{\mathrm{d}x} \qquad (4)$$

where C_1 and C_2 are the mass fractions of components 1 and 2 respectively. Using the notation of Ref. 8, the mass fraction C_1 is related to the more familiar mole fraction n_{10} by

$$C_1 = \frac{n_{10}M_1}{n_{10}M + n_{20}M_2} \text{ and } n_{10} = \frac{(C_1/M_1)}{(C_1/M_1)+(C_2/M_2)}$$

where M_1 and M_2 are the molar masses.

According to the linear thermodynamics of irreversible processes,[9] we may now write the phenomenological equations for the fluxes in terms of the thermodynamic forces:

$$J_\mathrm{q} = -\frac{L_\mathrm{qq}}{T^2}\frac{\mathrm{d}T}{\mathrm{d}x} - L_{\mathrm{q}1}\frac{(\partial\mu_1/\partial C_1)}{C_2T}\frac{\mathrm{d}C_1}{\mathrm{d}x} \qquad (5)$$

$$J_1 = -\frac{L_{1\mathrm{q}}}{T^2}\frac{\mathrm{d}T}{\mathrm{d}x} - L_{11}\frac{(\partial\mu_1/\partial C_1)}{C_2T}\frac{\mathrm{d}C_1}{\mathrm{d}x} \qquad (6)$$

In Eqs. (5) and (6), the forces and fluxes have been chosen from the expression(4) for the entropy production. The L's are the phenomenological coefficients. Although Truesdell has shown[10] that one cannot assume the validity of the Onsager reciprocal relations in general situations, it seems that we are justified in doing so here.[11] Thus,

$$L_{1q} = L_{q1} \tag{7}$$

The phenomenological equations, when heat conduction and diffusion are considered separately, become

$$J_q = -\frac{L_{qq}}{T^2}\frac{dT}{dx}$$

$$J_1 = -\frac{L_{11}(\partial\mu_1/\partial C_1)}{C_2 T}\frac{dC_1}{dx}$$

These equations may be compared with Fourier's law for heat conduction $[J_q = -\lambda(dT/dx)]$ and Fick's law for diffusion $[J_1 = -\rho D_{12}(dC_1/dx)]$ to yield expressions for the heat conductivity(λ) and diffusivity (D_{12}) coefficients:

$$\lambda = L_{qq}/T^2 \tag{8}$$

$$D_{12} = \frac{L_{11}(\partial\mu_1/\partial C_1)}{\rho C_2 T} \tag{9}$$

where ρ is the total mass density $(\rho = \rho_1 + \rho_2)$. We can also obtain a relationship involving the thermal diffusion factor by considering Eq. (6) [with $J_1 = 0$ in the stationary state] in conjunction with the difinition[7,8] $[(dC_1/dx) = -\alpha C_1 C_2 T^{-1}(dT/dx)]$ of the thermal diffusion factor, α. Thus,

$$L_{1q} = L_{11}(\partial\mu_1/\partial C_1)_{T,p} C_1 \alpha \tag{10}$$

We are now in a position to consider the Dufour effect. Suppose two gases (labelled with subscripts 1 and 2), initially at the same temperature, diffuse into each other. Equation (5), with the help of Eqs. (7), (8), and (9), then becomes:

$$J_q = -\lambda\frac{dT}{dx} - \rho_1\left(\frac{\partial\mu_1}{\partial C_1}\right)_{T,p} D_{12}\alpha\left(\frac{dC_1}{dx}\right) \tag{11}$$

From the difinition of J_q, it is apparent that it reduces to J_u in the limit when J_i approaches zero. By the conservation of energy, in the absence of convection, we have

$$\rho C_p\left(\frac{\partial T}{\partial t}\right) = -\frac{dJ_q}{dx}$$

where C_p is the constant pressure heat capacity of the mixture and $(\partial T/\partial t)$ is the variation of the temperature with time. Putting Eq. (11) into this equation, we obtain

$$\rho C_p\left(\frac{\partial T}{\partial t}\right) = \frac{d}{dx}\left[\lambda\frac{dT}{dx} + \rho_1\left(\frac{\partial\mu_1}{\partial C_1}\right)_{T,p} D_{12}\alpha\frac{dC_1}{dx}\right]$$

At the maximum temperature difference, ΔT_{max}, $(\partial T/\partial t) = 0$. This condition holds in general when

$$\lambda\frac{dT}{dx} + \rho_1\left(\frac{\partial\mu_1}{\partial C_1}\right)_{T,p} D_{12}\alpha\frac{dC_1}{dx} = K \tag{12}$$

where K is a constant which depends on the geometry of the diffusion apparatus (in particular, the position of the thermocouples) and must be determined experimentally. It is possible to leave $K=0$ as Rastogi and Madan[3] did, but this is not the most general case.

Equation (12) can be put into a form suitable for calculating the thermal diffusion factor, α, from the maximum temperature difference, ΔT_{max}. We shall assume that the gases which interdiffuse are ideal, in so far as the expression for the chemical potential is concerned:

$$\mu_1 = \mu_1^\circ(T) + \frac{RT}{M_1}\ln\left[P(C_1/M_1)/(C_1/M_1 + C_2/M_2)\right] \tag{13}$$

where μ_1° (T) is equal to a constant which is a function of temperature alone.

This equation may be substituted into Eq. (12) to give:

$$\lambda\frac{\Delta T}{\Delta x} + \frac{\rho_1 RTD_{12}\alpha}{C_1[M_1 - C_1(M_1 - M_2)]}\frac{\Delta C_1}{\Delta x} = K \tag{14}$$

where we have replaced differentials by finite changes, since the effect under consideration is very small (ΔT is written here in place of ΔT_{max}, and ΔT_{max} is usually less than 0.5 °C). Δx is the distance between the thermocouples.

Experimental

The apparatus used in the diffusion thermoeffect measurements was similar to that of Boushehri.[6] The apparatus consisted of two double-walled glass bulbs (50-ml capacity each) with a five junction thermocouple in each. The distance between the thermocouples (Δx) was 18.5 cm. The bulbs were connected *via* a stopcock having a bore of 8 mm in diameter. All runs were made at 25 °C under 700 Torr. The annular space between the double walls of the bulbs was evacuated to minimize heat loss. The maximum temperature difference between the thermocouples was obtained after the stopcock connecting the half cells was opened and interdiffusion was allowed to occur. The gases were supplied by the Fluka company and were used without further purification, since the results were not expected to be sensitive to small impurities. The minimum purity was at least 99.9%. The calculations were carried out at the Computer Center of Pahlavi University using the IBM 370 model 135.

Results and Discussion

Measurements were made at 25 °C and 700 Torr. It was observed that the temperature of the half-cell containing the lighter component always rose. The values of maximum temperature difference, $(\Delta T)_{max}$, are given in Table 1. No measurements of $(\Delta T)_{max}$ other than pure gases were carried out.

Equation (14) can be used to obtain α from ΔT_{max} provided that ΔC_1 is known together with the heat conductivity (λ), density (ρ_1) and diffusion coefficient (D_{12}). The apparatus constant K is usually eliminated by using a relative method, *i.e.* by performing the experiment with a pair of gases of known α. By knowing the time (typically a few seconds after initiating the diffusion process) at which ΔT reaches its

TABLE 1. DUFOUR EFFECT IN GASEOUS SYSTEMS AT 25 °C AND 700 Torr

Systems	$(\Delta T)_{max}$ (in °C)	Warm side
$H_2 + N_2$	0.17	Hydrogen
$H_2 + O_2$	0.14	Hydrogen
$H_2 + N_2O$	0.25	Hydrogen
$He + N_2O$	0.19	Helium
$He + O_2$	0.11	Helium

Table 2. Thermal diffusion factors for gas mixtures

Systems	α, from Equation (14)	α, from Equation (8.2—50) of Ref. 13	α, from thermal diffusion measurements
$H_2 + N_2$	0.35	0.348	0.35
$H_2 + O_2$	0.45	0.332	0.33[a]
$H_2 + N_2O$	0.40	0.312	0.48[b]
$He + N_2O$	0.36	0.391	—
$He + O_2$	0.34	0.386	—

a) The value of α for H_2+O_2 was estimated using Fig. 3 of Nain and Saxena.[14] b) The value of α, for H_2+N_2O was estimated using Table 1 of El Nadi and Faragi for mean temperature 368 K.[15]

maximum value after the start of the experiment, Fick's second law of diffusion[12] can be used to obtain ΔC_1, assuming that D_{12} is known for the gases concerned. For λ and ρ_1, the values for the pure component were used, since typical values of ΔC_1 were little different from unity. The apparatus constant K was calculated to be 2.72×10^{-5} by setting the value of α equal to 0.35 for hydrogen-nitrogen mixture.[12] Since the apparatus geometry remained the same in all experiments, this value of K was used in estimating α for the other systems. These are shown in Table 2. It may be noted that the Dufour effect gives the value of α at specific temperature which is in one respect an advantage compared to the thermal diffusion measurements. The values of thermal diffusion factors for equimolar mixtures obtained from Eq. (8.2—50) of the treatise of Hirschfelder *et al.*[13] with those obtained directly from thermal diffusion measurements are also given in Table 2. The values of α obtained from irreversible thermodynamics of the Dufour effects are subject to several sources of error such as convective mixing effects in our experiments or to the use of pure component values of λ and ρ_1 in Eq. (14). Since diffusion apparatus is employed (with only the addition of an appropriately placed thermocouples), it seems that this approach could provide information on both the diffusion coefficient and the thermal diffusion factor in the same series of experiments.

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