Estimation of Thermal Diffusion Factors in Gas Mixtures from Diffusion Thermoeffect Experiments. 4. Helium–Methane

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Measurements of the diffusion thermoeffect (the Dufour effect), using a modified Loschmidt apparatus, are reported for a helium–methane mixture at 35 °C and 760 torr. Maximum temperature differences have been obtained with the thermocouple at different positions from the diffusion interface. This work shows that the Dufour effect would be more pronounced at the surface of separation of the two gases. The values of thermal diffusion factors are estimated for the gas mixture from experimental data.

The diffusion thermoeffect in gases (the Dufour effect) is important because it is perhaps the least investigated of the transport properties of gases and because it shows considerable promise as a means of obtaining the values of gas transport properties, in particular the thermal diffusion factor. This effect involves the measurement of the transient temperature gradient which occurs in a diffusing fluid system as a result of an initial concentration gradient, and therefore it can be regarded as the inverse of thermal diffusion. The Dufour effect in gases was discovered by Dufour in 1872 (*6*) but not investigated until its rediscovery in 1942 by Waldmann (*5*). The possibility of the Dufour effect is contained in the Chapman–Enskog theory of nonuniform gases (*4*), but it is only recently that it has been experimentally investigated. Waldmann (*14*) did some experiments using a steady-state flow method. All the other workers (*1–3*, *10–13*, *15*) have employed a non-steady-state method with a Loschmidt-type apparatus, the one used in this study also. The essential features of a Loschmidt apparatus are a diffusion chamber consisting of two halves which can be separated in some way and a temperature-sensing device at a distance from the plane of initial separation of components. For the measurement of temperature gradient (which is a result of an initial concentration gradient) an apparatus similar to that used by Boushehri (*1*), with some modification to allow a variation in the position of the thermocouples, was constructed for the work discussed here. Apart from the classic studies of Waldmann and the work of Rastogi and Madan (*12*), very little work in this area has been done. Mason et al. (*10*) made an investigation of the pressure dependence of this effect, and recently a study of the temperature dependence of the diffusion thermoeffect was made by Boushehri (*1*). Sawford et al. (*13*) and Boushehri et al. have published more measurements (*2*, *3*).

When two transport processes take place simultaneously, they may interfere and produce cross phenomena. An example is interference of diffusion and heat conduction, which gives rise to diffusion thermoeffect. This effect is the temperature difference arising from a concentration gradient for two gases (labeled subscripts 1 and 2) at the same initial temperature diffusing into each other, a theoretical estimate of the expected Dufour effect can be made from irreversible thermodynamics (*2*). It can be shown that

$$\alpha = \frac{(K\Delta x - \lambda \Delta T)\{C_1[M_1 - C_1(M_1 - M_2)]\}}{\rho_1 RT D_{12} \Delta C_1} \quad (1)$$

where ΔT and Δx are the maximum temperature difference and the distance between thermocouple junctions, respectively, λ

and D_{12} are thermal conductivity and diffusivity coefficients, ρ_1 and C_1 are the mass density and mass fraction of component 1, respectively, M_1 and M_2 are the molar weights, and α is the thermal diffusion factor. K depends on the geometry of the cell (in particular, the position of thermocouples); K may be determined from experimental data. It is possible to leave $K = 0$ as Rastogi and Madan (*12*) did, but that would not be the most general case.

ΔT was measured by using cells in which the distances between thermocouple junctions were different. Sawford et al. (*13*) and Ingle et al. (*8*) showed the position dependence of temperature. K was estimated for each cell by using known data on thermal diffusion factor for a mixture of hydrogen and methane (*7*) and checked with an H_2–N_2 mixture obtained in previous work (*1*). To enable a comparison with the values obtained for α in earlier studies (*1*), it is preferable to choose H_2–CH_4 for calibration purposes. This value of K was used for the calculation of the thermal diffusion factor for other mixtures. The value of K was estimated for each cell, and it was found to increase with a decrease in the distance between thermocouple junctions.

Experimental Section

The apparatus used for the measurement of this work is essentially similar to that used by Boushehri (*1*) with appropriate modifications for changing the position of the thermocouples and with a different volume as dictated by the practical difficulties in making the apparatus. The apparatus consists of two double-walled half-cells having an inner tube 30 cm long in which the distances (*a*, *b*, *c*) between thermocouple junctions were 31, 41, and 51 cm, respectively. A five-junction thermocouple and Leeds and Northrup potentiometer (±1 μV) were used by which ΔT could be measured to ±0.005 °C. Thermocouples were parallel to the interface plane. The capacity of each half-cell was about 270 mL. The two half-cells were connected by a stopcock having a bore of 3.4 cm diameter. The diameter of the interfacial portion of this apparatus was equal to the cell diameter. The apparatus was thermostated by means of a water bath. The bath temperature was controlled to within ±0.05 °C. The apparatus was allowed to reach thermal equilibrium in the water bath with the temperature of 35 °C for 2 h. The annular space between the double walls of the cells was then evacuated to reduce heat conduction to the bath. It was allowed to remain for further 2 h to ensure constancy of temperature. When the stopcock is opened, diffusion of the two gases caused a temperature gradient across the two junctions of the thermocouple which was measured with the potentiometer. The maximum temperature change and time required for its attainment were recorded. This procedure was repeated for each gas mixture at the experimental conditions. For each mixture three runs were performed. The deviation from the mean was ±0.005 °C in all cases. The results are given in Table I.

Nitrogen was supplied by the Matheson Co. Helium, hydrogen, and methane were supplied by the Fluka Co. The minimum purities were 99.9%. The results were not expected to be sensitive to small impurities; therefore the gases were used without further purification.

Table I. Dependence of Dufour Effect on the Distance between Thermocouple Junctions

system	$(\Delta T)_{max}$, °C (±0.005)			α from eq 1			α from thermal diffusn measurmts	ref
	31.0 cm[a]	41.0 cm	51.0 cm	31.0 cm[a]	41.0 cm	51.0 cm		
$H_2 + N_2$	0.955	0.685	0.631	0.437	0.437	0.441	0.35	9
$H_2 + CH_4$	0.797	0.534	0.502	0.288	0.288	0.288	0.288	7
$He + CH_4$	0.903	0.578	0.534	0.155	0.157	0.158		

[a] Distance between thermocouple junctions.

Results and Discussion

The values of maximum ΔT observed are given in Table I. These are the mean of three observations. The uncertainty in ΔT is of order ±0.005 °C. This table shows that the Dufour effect would be more pronounced at the surface of separation of the two gases.

Equation 1 can be used to estimate the magnitude of α, provided that ΔC_1 and C_1 are known. The value of C_1 could not be measured directly, but it was estimated from Fick's second law of diffusion, which is written as (9)

$$C_t = \frac{1}{2}C_0\left[1 - \text{erf}\frac{X}{2(Dt)^{1/2}}\right] \qquad (2)$$

where D is the diffusion coefficient, X, taken to be equal to $^1/_2\Delta X$, represents the distance between the thermocouple and the plane of initial separation of components, t is time (typically a few seconds after initiating the diffusion process) when ΔT reaches a maximum value and is obtained from experiment, C_t is the concentration of the particular component in the second chamber at time t, and C_0 is the concentration of that component in the original chamber.

By use of the value of the time t, obtained in the present investigation, and the known value of the diffusion coefficient, ΔC_1 was found to be close to unity. Thus it follows that $\Delta C_1 = C_0$ in the present case. K was estimated for each cell by using the known value of the thermal diffusion factor $\alpha = 0.288$ for hydrogen–methane mixtures. This value of K was used for calculation of the thermal diffusion factors for other mixtures. The results are recorded and compared in Table I. No measurements other than those for the pure gases were recorded.

H_2–CH_4 was chosen for calibration purposes in order to be able to compare our present results with the results in ref 1, where both systems H_2–CH_4 and H_2–N_2 were reported among others. The calculated value of α for H_2–N_2 based on an assumed value of $\alpha = 0.288$ for H_2–CH_4 in the present work, Table I, is almost identical with the value of 0.44 reported earlier in ref 1. The reason we chose H_2–N_2 rather than H_2–CH_4 for calibration in the study reported in ref 2 was that the systems we investigated did not include H_2–CH_4.

In Table I the value of the thermal diffusion factor for H_2–N_2, obtained directly from thermal diffusion measurements, is shown for comparison purposes. This value is of the correct order of magnitude but does not agree precisely with that obtained from our experiments. We have indicated the error range of ΔT (±0.005 °C) in Table I. The error in α, however, cannot be obtained on the basis of this error in ΔT alone, since as is apparent from eq 1, considerable uncertainty enters the calculated value of α because of the convective mixing effects in our experiment and because of the uncertainties in λ and ρ_1. The values of λ and ρ_1 are not known for the mixtures, forcing us to use, as an approximation, their values for pure gases.

Thermal diffusion factor α, obtained from Dufour effect measurements in the case of H_2–N_2 mixtures, is bigger than that obtained from thermal diffusion experiments by a factor of 1.26. It might be considered plausible that in the case of He–CH_4 mixtures, the value of α obtained from the above two experimental methods should exhibit a discrepancy of the order of
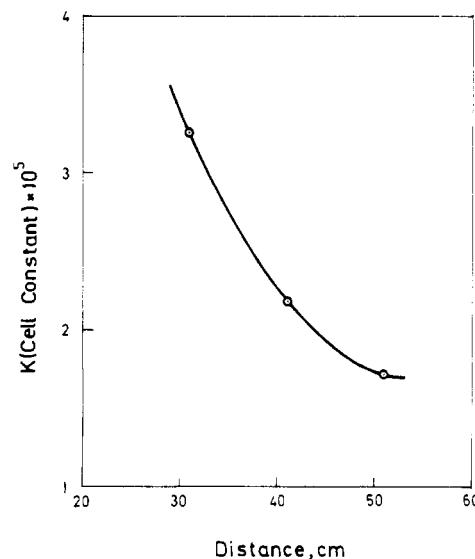

Figure 1. Dependence of K on the distance between thermocouple junctions.

26%. Because of the lack of data from thermal diffusion experiment, nothing definite can be concluded.

The values of K estimated for each cell are plotted in Figure 1. K is found to increase with a decrease in the distance between the thermocouple junction and the plane of initial separation of the components. It should also depend on the mixture studied since the composition dependence of both α and the thermal conductivity are quite important (10). However, at present, there is no satisfactory theory for K.

The interpretation of the diffusion thermoeffect is more complicated than thermal diffusion since there is heat conductivity involved in the former but not in the latter. This is the disadvantage of this method compared to thermal diffusion measurements. On the other hand, the Dufour effect gives the value of α at specific temperatures.

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