BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (7), 2097—2098 (1979)

Diffusion Thermoeffect in Gases (The Dufour Effect)

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(Received July 24, 1978)

A study of the Dufour effect was made for four different gas mixtures: SF_6–N_2O, SF_6–N_2, SF_6–CO_2, and He–CO_2. Measurements were made at 300 K under 700 Torr. The values of the thermal diffusion factor were calculated for the above mixtures from experimental data on the basis of the thermodynamics of irreversible processes. A theoretical study was made also to calculate the thermal diffusion factor from kinetic theory.

The diffusion thermoeffect arises when a concentration gradient exists in a gas mixture. This gradient leads to a transient nonuniform temperature. Therefore, this effect is related to thermal diffusion, where a concentration gradient arises as a result of an initial temperature gradient. The thermal diffusion factor can be obtained from the diffusion thermoeffect which is a supplement to the more usual methods of measuring thermal diffusion factors.[1)]

The Dufour effect[2)] was not extensively investigated until after its rediscovery by Waldmann in 1942.[3)] Although the possibility of this effect is contained in the Chapmann-Enskog theory[4)] of non-uniform gases, only recently have its experimental measurements been made. For the measurement of the temperature gradient (which is a result of an initial concentration gradient) an apparatus similar to that used by Boushehri and Afrashtehfar[5)] was constructed for the work discussed here. Apart from Rastogi and Madan's work,[6)] and the classic studies of Waldmann, very little work in this area has been done. Mason *et al.*[7)] made a study of the pressure dependence of this effect and, more recently, Sawford *et al.*[8)] and Boushehri[5,9)] have published more measurements. There is obviously a need for further independent studies, both to verify and to extend these few experimental studies.

Suppose two gases (labelled with subscripts 1 and 2), initially at the same temperature, diffuse into each other. On the basis of irreversible thermodynamics,[5,10)] it may be shown that

$$\frac{\rho_1 RTD_{12}\alpha}{C_1\{M_1-C_1(M_1-M_2)\}}\frac{\Delta C_1}{\Delta X}+\lambda\frac{\Delta T}{\Delta X}=K, \qquad (1)$$

where ρ_1 and C_1 are the mass density and mass franction of component 1, respectively; α is the thermal diffusion factor; λ and D_{12} are heat conductivity and diffusivity coefficients, respectively; M_1 and M_2 are the molar weights; ΔX is the distance between thermocouples; and ΔT is the maximum temperature difference. K is a constant which depends on the geometry of the cell (in particular, the position of thermocouples); K has to be experimentally determined from experimental data. It is possible to leave $K=0$ as Rastogi and Madan[6)] did, but this would not be the most general case.

Thermal diffusion factors have been estimated from the experimental data. Calculations for the first approximation to the thermal diffusion factor in binary mixtures was done on an IBM 370 model 135 computer for all four systems to check the values of the thermal diffusion factors deduced from Dufour effect against the values predicted by the Chapmann-Enskog kinetic theorv. The experimental value for the thermal diffusion factor is comparable with its theoretical value for equimolar mixtures.

Experimental

The apparatus employed was similar to that used by Boushehri and Afrashtehfar.[5)] The apparatus consisted of two double-walled glass bulbs (1, 2) of capacity 50-ml each. The two half-cells were connected by a narrow tube via stopcock having a bore of 8 mm diameter. A three junction thermocouple and a Leeds and Northrup potentiometer (±1 μV) was used by which ΔT could be estimated to ±0.01 °C. The thermocouples were parallel to the diffusion interface. The distance between two thermocouples was equal to 18.5 cm. The apparatus was kept in an oil bath. The temperature of bath was controlled to ±0.1 °C. The apparatus was kept in a thermostat for two hours to insure thermal equilibrium. The annular space between the double walls of the bulbs was then evacuated to minimize heat dissipation. The apparatus was allowed to remain for further two hours to insure constancy of temperature. When the stopcock connecting the two half-cells was opened, diffusion of the gases caused a temperature gradient. This was measured as indicated above.

SF_6, N_2, and CO_2 were supplied by the Matheson Co. He and N_2O were supplied by the Fluka Co. The gases were used without further purification, since the results were not expected to be sensitive to small impurities. The purity was at least 99.9%.

Results and Discussion

The mixtures studied were: SF_6–N_2O, SF_6–N_2, SF_6–CO_2 for which the Dufour effect has not been measured previously. A CO_2–He mixture was used to determine the apparatus constant. Thermo-emf was measured using a three junction thermocouple in conjunction with the potentiometer. The temperature of the half-cell containing the lighter component always rose. The values of maximum temperature $(\Delta T)_{\max}$ are given in Table 1. No measurement of $(\Delta T)_{\max}$ other than for pure gases were made.

The diffusion thermoeffect is of interest in its own right and because it enables us to obtain quantitative information of the other transport coefficients, especially the thermal diffusion factor. An explicit derivation of the thermal diffusion factor on the basis of irreversible thermodynamics is given in Ref. 5. All measurements were made at 300 K and 700 Torr.

From irreversible thermodynamics the relationship between the temperature gradient and concentration gradient is shown by Eq. 1, where K is an apparatus

Table 1. Dufour effect in gaseous systems at 300 K and 700 Torr

System	$(\Delta T)_{\max}$ in K($\pm$0.01)	Warm side
$He+CO_2$	0.11	He
N_2+SF_6	0.12	N_2
N_2O+SF_6	0.16	N_2O
CO_2+SF_6	0.18	CO_2

Table 2. Comparison of the values of α for different systems

System	α, from Eq. 1	α, from thermal diffusion measurement	α, from Equation (8.2—50) of Ref. 12
$He+CO_2$	0.42	0.45[a]	0.398
N_2+SF_6	0.13	—	0.192
N_2O+SF_6	0.12	—	0.073
CO_2+SF_6	0.12	—	0.075

a) The value of α was obtained using Table 2 of Boushehri.[9)]

constant which depends on the position of thermocouples and the geometry of the cell. It may be possible to get an expression for this constant by studying variation of ΔT with both position of thermocouples and the geometry of the cell. Equation 1 can be used to estimate the value of α from the values of $(\Delta T)_{\max}$ provided that ΔC_1 is known. ΔC_1 can be obtained by using the integrated form of Fick's second law of diffusion,[11)] which is given by

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

D is the diffusion coefficient and t is the time in seconds when reaches a maximum value and is known from experiment. C_t is the concentration of the particular component in the second chamber at time t, C_0 is the concentration of the component in the original chamber, and X is the distance from thermocouple to the plane of initial separation of components. For λ and ρ_1 in Eq. 1, we had some difficulty in assigning the values since these were not known at various concentrations. Therefore, the values for pure components were used. By setting the value of $\alpha=0.45$ for carbon dioxide–helium mixture in Eq. 1, the apparatus constant K was estimated to be 3.05×10^{-5}. This point was not considered by Rastogi and Madan who left $K=0$ in their work. Since the distance between two thermocouples was the same in all experiments, this value of K was used for calculation for other systems. The values of α obtained in this way are recorded in the second column of Table 2. These are of the same order of magnitude as the values of thermal diffusion factors for equimolar mixture obtained from Equation (8.2—50) of the treatise of Hirschfelder *et al.*[12)] (Column 4).

In our system, a rather large concentration gradient was present which may be eliminated by taking a binary mixture in two half cells instead of pure gases. Also there was a convective mixing effect. In choosing the values of λ and ρ_1 in Eq. 1 there was some arbitrariness, the values of these parameters used being the values of the pure components.

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 the thermal diffusion measurements. On the other hand, the Dufour effect gives the value of α at specific temperatures. In short, this method shows considerable promise as a means of obtaining the value of gas transport coefficients.

We thank the Iranian Ministry of Higher Education Research Foundation and the Department of Chemistry of Shiraz University for the research facilities.

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