ence between the stagnation and static pressure was measured directly with the pressure transducer. (The static pressure was the submergence of the tube, 1.5 in.) For the range of velocities used in the program, the pressure coefficient was independent of velocity. It is apparent from Figure 1 that as the concentration of the polymer is increased beyond a certain value, the sensitivity of the impact tube is drastically decreased. This effect is more pronounced for the smaller flattened tube, 3S, as reduction in the pressure coefficient is noted for concentrations greater than 25 wt. p.p.m. For the larger flattened tube, 2S, reduction is not noted until the concentration exceeds 100 wt. p.p.m. The response of the tube with a hemispherical head, 1R, was essentially the same as that of the larger flattened tube. It is felt that the effect noted here is not due to purely viscous effects, as the trend is in the opposite direction from that previously reported (*4*) for viscous Newtonian fluids. Also, the apparent viscosities of the aqueous polymer solutions were not greatly different from water.

The results indicate that extreme caution must be exercised in utilization of impact tubes in the measurement of velocity in polymer solutions. More extensive investigations should be carried out to clarify further the observed phenomenon.

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Dufour Effect in Liquid Systems

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The interaction between thermal and mass fluxes has long been recognized. Much effort has been devoted to the study of thermal diffusion (*6, 7, 8*). Its practical importance has been highlighted by the successful application of a thermal diffusion (Soret effect) process to the purification of uranium isotopes (*5*). Yet little or no attention has been paid to its counterpart, the Dufour effect, which represents the contribution to the energy transfer resulting from the mass fluxes. This is especially true for liquid systems. Statements have appeared repeatedly in the literature (*1, 10*) that the Dufour effect in liquid systems is usually assumed to be of minor importance. Unfortunately, these statements which were based only on a few experiments with binary systems, tended to discourage any real attempt to investigate the nature of such a phenomenon.

A recent study (*3*) of the general problem of nonisothermal multicomponent diffusion in the liquid phase has revealed that a significant Dufour effect may accompany diffusion in a liquid phase. A brief summary of this finding is given here.

FLUX REPRESENTATION

The general formulation of the nonisothermal diffusion problem is available elsewhere (*3*). Thus, only the resulting equations pertaining to the present discussion will be presented below.

For a multicomponent system, the unidirectional flux equations for the mass and heat transfer may be combined in a single form as

$$j_\alpha = -\sum_{i=1}^{n} D_{\alpha i}\frac{\partial \tau_i}{\partial x} \qquad \alpha = 1,2, \ldots n-1, n \tag{1}$$

The indices 1 to $(n-1)$ designate the $(n-1)$ independent mass concentrations and fluxes while the index n refers to the thermal components (that is, $\rho C_p T$ and heat flux). If the transport process is restricted to a semi-infinite medium with fixed concentrations and temperature at its boundary, and constant physical properties and transport coefficients, then the diffusion equations can be uncoupled and solved using a linear transformation (*9*) as

$$\sum_{i=1}^{n} D_{\alpha i}\, Q_{i\beta} = \lambda_\beta\, Q_{\alpha\beta} \tag{2}$$

In Equation (2), the $Q_{\alpha\beta}$ are elements of a real matrix which diagonalizes the matrix of transport coefficients (*3*), and the λ_β are the positive real eigenvalues. The

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solutions for the concentration and temperature profiles are

$$[\tau_\alpha{}^o - \tau_\alpha\,(x,t)] = \sum_{i,j,k=1}^{n} Q_{\alpha i}\delta_{ij} \left\{ \frac{\operatorname{erf}\left(\dfrac{x}{2\sqrt{t\lambda_i}} - \dfrac{\lambda}{\sqrt{\lambda_i}}\right) + \operatorname{erf}\left(\dfrac{\lambda}{\sqrt{\lambda_i}}\right)}{1 + \operatorname{erf}\,(\lambda/\sqrt{\lambda_i})} \right\} Q_{jk}{}^{-1}\,(\tau_k{}^o - \tau_k{}^\infty) \quad (3)$$

where λ is a constant determined by the convective velocity of the system, the $\tau_\alpha{}^o$ are the concentrations and temperature at the phase boundary ($x = 0$), and the $\tau_\alpha{}^\infty$ are the initial concentrations and temperature. For the case of diffusion in an isothermal ternary system without convection, Equation (3) reduces to the results obtained by Fujita and Gosting (*4*).

NUMERICAL EXAMPLE

Based on Equations (1) and (3), numerical calculations have been carried out for a fictitious five component system that resembles a hydrocarbon mixture. Realistic values were assigned to the independent diffusion coefficients based on binary and ternary data. Such a basis was justified on the assumption of a dilute solution. The Soret coefficients were also estimated from known data. They are in the range of 10^{-9} to 10^{-7} $\left(\dfrac{\text{sq.cm.}\cdot\text{g.}}{\text{sec.}\cdot\text{cal.}}\right)$. The Dufour coefficients and the dependent mass diffusion coefficients were calculated to satisfy the Onsager reciprocal relations (*2*). It is significant to note that the Dufour coefficients thus obtained were as large as 10^{-2} $\left(\dfrac{\text{sq.cm. cal.}}{\text{sec.}\cdot\text{g.}}\right)$. These values appear to be much larger than expected. They are certainly contrary to the common belief that the Dufour effect in the liquid phase is negligible.

Calculations were carried out, using Equation (3), for thermal transfer characteristics. The initial mass concentrations were taken to be zero while constant boundary concentrations, ranging from 0.01 to 0.04 (g./cc.), were assigned. The results of three typical cases (*3*) are presented here.

Case I

Both the initial and the boundary temperature were taken to be 300°K. The Soret coefficients were in the range of 10^{-9} to 10^{-8} $\left(\dfrac{\text{g.}}{\text{cal.}}\cdot\dfrac{\text{sq.cm.}}{\text{sec.}}\right)$. The calculated temperature profile was observed to increase from the boundary to a maximum value of 300.3°K. at $x/2\sqrt{t} = 0.0075$ and then to gradually decrease to the initial value. This temperature inversion phenomenon is clearly a manifestation of the Dufour effect in the region of high concentration gradients.

Case II

The Soret coefficients used for this case were increased by a factor of ten which produced a tenfold increase in the Dufour coefficients (*3*), while all other conditions were maintained the same as in Case I. The maximum in the temperature profile increased to 303.1°K. at $x/2\sqrt{t} = 0.0035$. This indicates that the magnitude of the maximum temperature rise serves as a quantitative representation of the Dufour effect.

Case III

The initial temperature was fixed at 290°K. (that is, 10°K. below the boundary temperature) with all other parameters identical to Case I. No maximum temperature was noted in the temperature profile for this case. The Dufour effect was essentially masked by the large overall thermal gradient of 10°K. imposed on the system.

A more dramatic display of the Dufour effect is illustrated in Table 1 where the normalized Dufour contributions to the thermal flux are compared for the three cases. The large positive values of the Dufour contribution for Cases I and II indicate that the direction of the thermal flux opposes the thermal gradient and that the complementary Fourier contribution is negative. The magnitude of the Dufour contribution becomes unity at precisely the location where the maximum temperature occurs. For Case III, since there is no maximum in the temperature profile, the Dufour flux is always much less than total thermal flux as indicated by the small values of the normalized Dufour contribution. In other words, the heat transfer process is essentially unaffected by the mass transfer in this case.

TABLE 1. NORMALIZED DUFOUR CONTRIBUTION

$$1 + \left[\left(D_{55}\frac{\partial\tau_5}{\partial x}\right)/j_5\right]$$

$x/2\sqrt{t}$	Case I	Case II	Case III
0	7.11	11.43	0.18
0.002	6.30	5.65	0.17
0.0035	—	1.00	—
0.004	3.86	0.71	0.12
0.006	1.88	0.30	0.067
0.0075	1.00	—	—
0.008	0.80	0.17	0.032
0.010	0.31	0.10	0.013
0.012	0.11	0.06	0.005

CONCLUSIONS

The finding of a strong Dufour effect in the liquid phase is contrary to common belief. Under realistic physical conditions, the Dufour effect could conceivably produce a significant and measurable temperature inversion even in a dilute liquid system. This points to a practical means for accurate determination of the Dufour as well as the thermal diffusion coefficients. It also suggests possible experimental verification and measurement of a phenomenon that has been ignored in the past.

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