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The Dufour effect. II. Experimental confirmation of the Onsager heat-mass reciprocal relation for a binary liquid mixture

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tion experiments, one obtains with rigid activated complexes⁶ the values shown in Fig. 1. Although these values of $k(E)$ disagree with the experiments by about a factor of 2, the absolute magnitude and the changes for various substituents are in satisfactory agreement. More sophisticated statistical models with less rigid complexes can be designed to represent the experiments more quantitatively.

We may conclude that with the present technique specific rate constants $k(E)$ of simple unimolecular processes can be measured directly in a time resolved way. The results are of basic importance for unimolecular rate theory.

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The Dufour effect. II. Experimental confirmation of the Onsager heat-mass reciprocal relation for a binary liquid mixture

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Although experimental verification of Onsager's reciprocal relations has been achieved in a variety of cases,¹ no quantitative test of the heat-mass reciprocal relation for a binary liquid system has previously been reported. We present in this communication experimental proof of the equality of the mass-heat reciprocal relation for the system carbon tetrachloride-cyclohexane.

The linear relations between fluxes and independent forces for a binary, isotropic, nonelectrolyte liquid system are²

$$-\mathbf{q} = \Omega_{00} \nabla \ln T + \Omega_{01} \nabla_T (\bar{\mu}_1 - \bar{\mu}_2), \quad (1)$$

$$-\mathbf{j}_1 = \Omega_{10} \nabla \ln T + \Omega_{11} \nabla_T (\bar{\mu}_1 - \bar{\mu}_2), \quad (2)$$

where \mathbf{q} is the heat flux, \mathbf{j}_1 is the diffusion flux, $\bar{\mu}_\alpha$ is the specific chemical potential of component α , $\nabla_T \bar{\mu}_\alpha \equiv \nabla \bar{\mu}_\alpha + \bar{S}_\alpha \nabla T$ (\bar{S}_α is partial specific entropy), and the

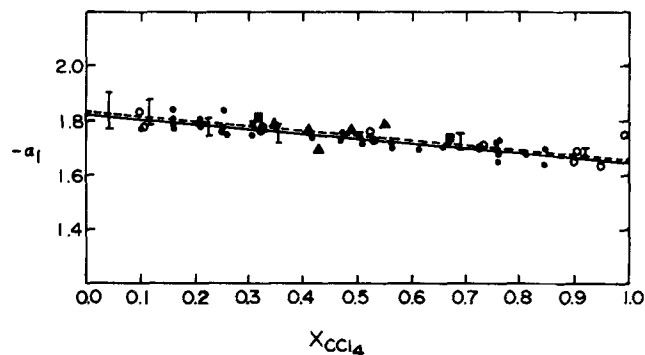


FIG. 1. Thermal diffusion factor at 25°C as a function of composition. Method of measurement is in parentheses. \blacktriangle , this work (Dufour effect); \diamond , Anderson and Horne⁶ (pure thermal diffusion); $- - I - -$, Stanford and Beryerlein⁷ (thermogravitation); \circ , Turner, Butler, and Story⁸ (flow cell); \blacksquare , Korchinsky and Emery⁹ (thermogravitation).

TABLE I. Heat of transport and Onsager coefficients for carbon tetrachloride-cyclohexane.

$\langle x_1 \rangle^a$	Δx_1^b	T °C	$Q_1^*/\text{kJ mol}^{-1}$ ($\sigma = 0.12$ kJ mol^{-1})	$\Omega_{01}^c/10^{-7}$ $\text{kg m}^{-1} \text{sec}^{-1}$ ($\sigma = 0.14 \times 10^{-7}$ $\text{kg m}^{-1} \text{sec}^{-1}$)	$\Omega_{10}^d/10^{-7}$ $\text{kg m}^{-1} \text{sec}^{-1}$ ($\sigma = 0.11 \times 10^{-7}$ $\text{kg m}^{-1} \text{sec}^{-1}$)	$(\Omega_{01} - \Omega_{10})/10^{-7} \text{kg m}^{-1} \text{sec}^{-1}$
0.3469	0.5933	22.21	5.47	6.35	6.26	0.09
0.4112	0.7865	23.01	5.59	6.48	6.43	0.05
0.4295	0.6687	21.98	5.43	6.14	6.34	-0.20
0.4843	0.8185	22.87	5.84	6.38	6.28	0.10
0.5514	0.7160	23.28	6.13	6.16	5.96	0.20

^aMean mole fraction of CCl_4 .

^bInitial difference in mole fraction of CCl_4 .

^cCalculated from first of Eqs. (3).

^dCalculated from second of Eqs. (3); thermal diffusion factors are averages of those from Refs. 6, 7, and 8 adjusted to the given temperature according to Ref. 6.

$\Omega_{\alpha\beta}$ are the Onsager coefficients. The reciprocal relation is $\Omega_{01} = \Omega_{10}$. The validity of this relation can be tested by a comparison of data obtained in two ways: (a) Measurement of the heat flux or the temperature gradient produced in an initially isothermal mixture by diffusion (Dufour effect) and (b) Measurement of the diffusion flux or the composition gradient produced by a temperature gradient in a mixture of initially uniform chemical potential (thermal diffusion).

To investigate the Dufour effect in liquids, an adiabatically insulated glass cell was constructed which allowed the creation of an initially sharp, unperturbed interface by the slow withdrawal of a third component from between the upper and lower layers. Distilled water was used as the middle layer because of its immiscibility with both carbon tetrachloride and cyclohexane (solubility less than 0.02 wt%).³ Temperature changes were monitored by copper-constantan thermocouple combs above and below the interface. The only previously reported attempts to measure the Dufour effect in liquids were by Rastogi *et al.*⁴ The diameter of the interfacial portion of their apparatus was half the cell diameter. This left a diathermic sheath of liquid above and below the interface. Such geometry is not amenable to theoretical analysis.⁵ Moreover, our experiments show that such a sheath greatly diminishes the ensuing temperature gradient because of thermal conduction.

Insertion of Eqs. (1) and (2) into the hydrodynamic equations of mass, momentum, and energy balance produces three coupled differential equations describing the Dufour effect.⁵ In the work reported here, we have used numerical solutions of the differential equations. The heat of transport Q_1^* is an adjustable parameter in our numerical scheme, and the heat of mixing and the thermal conductivity are fully included. A nonlinear least squares fit of the time dependent temperature difference between symmetric points about the interface

yields the "best" values for Q_1^* reported in Table I.

The heat of transport Q_1^* is related to the Onsager coefficient Ω_{01} , and the thermal diffusion factor α_1 is related to Ω_{10} , by²

$$\Omega_{01} = \rho D Q_1^* w_2 (\partial \bar{\mu}_1 / \partial w_1)_{T,P}^{-1}, \quad \Omega_{10} = -\alpha_1 w_1 w_2 \rho D, \quad (3)$$

where w_α is weight fraction of component α , ρ is density, and D is mutual diffusivity. As shown in Table I, Ω_{10} and Ω_{01} are equal within the estimated standard errors.

Having established the validity of the heat-matter Onsager reciprocal relation, we may calculate thermal diffusion factors from experimentally determined heats of transport. The results of the calculation are compared with literature values of directly determined thermal diffusion factors in Fig. 1. The thermal diffusion factors calculated from heats of transport are adjusted to 25°C.⁶

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