Soret Coefficient of Liquified Simple Gases at Low Temperatures: the Kr-CH_4 System

D. Longrée, J. C. Legros, and G. Thomaes

Université Libre de Bruxelles, Belgium

(Z. Naturforsch. **32 a**, 1061–1062 [1977];
received June 10, 1977)

The Soret coefficient for the krypton-methane system at 107.5 K has been measured. The results are compared with the thermodynamic theory of Prigogine, with a Rice Allnatt calculation, and with the Enskog theory for dense hard spheres gases.

As far as we know the Soret phenomenon, this is the partial separation of the components of a binary solution under the influence of a heat flux, has not yet been measured for liquid solutions of simple molecules at low temperatures (except for the He^4-He^3 system [1]). We present in this paper own results on the Kr-CH_4 system at 107.5 K for six different concentrations.

The maximum mass fraction difference (ΔN) measured at steady state between hot and cold plates is given by

$$\Delta N = -(D'/D)\, N(1-N)\, \Delta T$$

where D'/D is the Soret coefficient. In the usual cases, D'/D is small ($\approx 10^{-3} - 10^{-2}$) and the observed concentration changes are small and difficult to measure, the main problem being to have a convection-free layer of the solution subjected to a strictly vertical temperature gradient of known magnitude.

One of the aims of the experiments reported here was to test the theoretical suggestion, based on the work of I. Prigogine et al. [2] and of Denbigh [3], that the component with the higher heat of vaporisation per unit of volume should migrate towards the cold wall. One knows that this prediction fails for systems of organic liquids such as benzene-carbon tetrachloride [4]. The sphericity of the molecules that we used allowed us also to test the validity of the Rice-Allnatt theory [5] and to compare with the dense hard sphere gas theory of Enskog [6].

The cell essentially consists of a cylinder, 1 cm in height and 1 cm in diameter, filled with 125 vertical thin walled tubes in order to protect the system against convection. The top and bottom of the cylinder are maintained at different constant temperatures by means of a liquid nitrogen cryostat. The temperatures are measured with vapor pressure and platinum resistance thermometers.

The separation of the components between the top and bottom of the cell is measured by means of the variation of the dielectric constant of the liquid. (A calibration gives us the dependence of the dielectric constant on temperature and concentration.)

Figure 1 shows the variation of the capacity at the bottom of the cell as a function of time during a typical run.

Table I gives the results obtained for six different mass fractions.

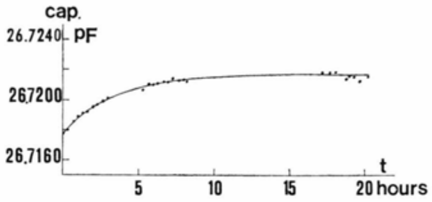

Fig. 1. Variation of the capacity as a function of time for run 3.

Table I.

Run	$N_{CH_4}^{\text{initial}}$	C^{initial} bottom (pF)	C^{steady} bottom (pF)	ΔT (K)	$\langle T\rangle^{\text{steady}}$	ΔN	$D'/D \times 10^2$ (K^{-1})	Prigogine [1]	$D'/D \times 10^2$ at 115 K by Rice-Allnatt theory [4]	$D'/D \times 10^2$ at 115 K dense hard spheres [5]
1	0.1921	26.8088 ±0.0001	26.8120 ±0.0001	4.704	107.483	0.0056	0.77 *	$D'/D > 0$		
2	0.1371	26.8726	26.8771	5.038	107.504	0.0053	0.89			
3	0.3035	26.7179	26.7218	4.932	107.443	0.0102	0.97			
4	0.1613	26.8748	26.8791	4.556	107.457	0.0060	0.97		4.6 (molar fraction = 0.5)	8.3 (molar fraction = 0.5)
5	0.3982	26.6218	26.6254	5.037	107.483	0.0122	1.01			
6	0.5031	26.5951	26.5979	4.724	107.475	0.122	1.03			

* By definition, $D'/D > 0$ when the denser component migrates towards the cold plate. Kr migrates towards the cold plate.

Reprint requests to Dr. J. C. Legros, Service de Chimie Physique E.P., Faculté des Sciences Appliquées, Université Libre de Bruxelles, 50, av. F. D. Roosevelt, *B-1050 Bruxelles*, Belgium.

The position of the points enables a least squares calculation of the linear relation

$$D'/D = a_0 + a_1 N_{\mathrm{CH_4}}$$

giving $a_0 = 8.137\ 10^{-3}$ and $a_1 = 4.468\ 10^{-3}$ (cf. Figure 2). We have been limited to $N_{\mathrm{CH4}} = 0.5$ at this temperature, because our apparatus cannot work at pressures much higher than one atmosphere.

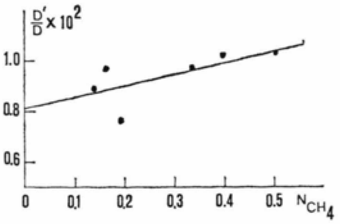

Fig. 2. D'/D as a function of the mass fraction of methane.

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[1] H. Dandache and J. P. Laheurte, J. Phys. (France) **34,** 635 [1973].

[2] I. Prigogine, L. de Brouckere, and R. Amand, Physica **16,** 577 [1950].

[3] K. G. Denbigh, Trans, Faraday Soc. **48,** 1 [1952].

[4] L. Guczi and H. J. V. Tyrrell, J. Chem. Soc. **1965,** 6576.

[5] C. C. Wei and H. T. Davis, J. Chem. Phys. **45,** 2533 [1966].

[6] S. Chapman and T. G. Cowling, Mathematical Theory of Non Uniform Gases, University Press, Cambridge 1939.