essure*

The Effect of Pressure on Diffusion in the System CCl4-SnI4*

E. P. <u>Doane</u> and H. G. Drickamer Department of Chemistry, University of Illinois, Urbana, Illinois (Received March 16, 1953)

Diffusion coefficients have been measured for the system CCl₄-SnI₄ using I¹³¹ tagged SnI₄. Isotherms were obtained at 50°C and 75°C to 2000 atmospheres pressure. The results are interpreted in terms of the activation enthalpy, entropy, and volume. Below 1000 atmospheres the diffusion mechanism differs only slightly from that in effect at atmospheric pressure. At higher pressures orientational effects are observed.

e highest denhese densities,

s pressure. In

 $12\pi n\sigma^3 + 0.1275 (\pi n\sigma^3)^2$ for solid elastic spheres.

pefficients are listed in I with theory. The p-r-f re used. It can be seen except at the highest perimental coefficients edicted by Eq. (1). In s-half times the critical

CH4-TCH3.

3.65 3.50 2.46 2.36 1.60 1.64 1.13 1.22 0.94 0.93 0.664 0.715 2.91 2.91 1.98 1.90 1.38 0.91 0.87 0.91 0.69 0.715 0.71 0.715 0.57 0.56 0.368 0.374 0.21 0.231 5.3 5.5 2.48 2.55 1.51 1.52 1.09 1.02 0.75 0.734 0.575 0.535 0.40 0.413 0.248 0.270 0.150 0.177	D _{expt} ×10 ² cm ² /sec	D _{theor} × 10 ⁴ cm ² /sec
	2.46 1.60 1.13 0.94 0.664 2.91 1.98 1.38 0.98 0.87 0.69 0.71 0.57 0.368 0.21 5.3 2.48 1.51 1.09 0.75 0.40 0.248	2.36 1.64 1.22 0.93 0.715 2.91 1.90 1.36 0.91 0.715 0.715 0.56 0.374 0.231 5.5 2.55 1.52 1.02 0.734 0.535 0.413 0.270

would be significant. tion to be expected.

o the previously pubred marked deviations cal density. This emaple CO₂ diffusion. Since symmetrical no such

icknowledge financial Energy Commission. Am. Chem. Soc, 53, 394 In a series of previous papers¹⁻⁴ a method was presented for measuring diffusion in liquids under pressure. This method was applied to organic liquid mixtures involving CS_2 as one of the components, and to aqueous solutions. The results were interpreted in terms of the activation enthalpy ΔH^{\pm} , the activation column ΔV^{\pm} , and the activation entropy above that at atmospheric pressure $\Delta S^{\pm} - \Delta S_0^{\pm}$.

This paper presents the results of measurements of diffusion of a very dilute solution of SnI₄ (I¹³¹ tagged) in CCl₄. The system was chosen because of the simple symmetry of the molecules. The tagged SnI₄ was prepared from iodine received as NaI from the Oak Ridge National Laboratory. I₂ was generated by

TABLE I. Diffusion coefficients SnI₄¹³¹ in CCl₄ - SnI₄ in CCl₄.

Temperature (°C)	Pressure (atmos)	Observed $D \times 10^{5}$ (cm ² /sec)
50	200	3.30
50	400	2.66
50	600	2.17
50	600	2.08
50	1200	1.12
50	2000	0.70
75	200	4.66
7.5	500	3.27
75	600	3.08
75	1000	1.97
75	1000	1.93
75	1500	1.24
75	2000	1.18
75	2000	1.06

heating with K₂Cr₂O₇, and this was reacted with metallic tin in CCl₄ solution as described by Mc-Dermott.⁵ The nonradioactive solution was matched colorimetrically with the tagged solution. All mixtures were carefully shielded from light to retard decomposition of the iodine. Two isotherms were obtained, at

*This work was supported in part by the U. S. Atomic Energy

¹ R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 267 (1953).

¹R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 575

Cuddeback, Koeller and Drickamer, J. Chem. Phys. 21, 589

R. B. Cuddeback, and H. G. Drickamer, J. Chem. Phys. 21, 707 (1953)

F. A. McDermott, J. Am. Chem. Soc. 33, 1963 (1911).

50°C and 75°C. The pressure range was limited to 2000 atmospheres because of freezing of CCl₄. The results are presented in Table I and Fig. 1.

The plot of D versus pressure shows a relatively constant decrease up to 1000 atmos. Beyond this point the rate of decrease slows gradually. In the plots of the ratio of the activation volume to the molal volume, $\Delta V^{\pm}/\bar{V}$, the activation enthalpy ΔH_p^{\pm} , and the increase in activation entropy from 1 to P atmospheres ΔS_p^{\pm} $-\Delta S_0^{\dagger}$ versus pressure (Figs. 2 and 3), this apparent change at about 1000 atmos is much more pronounced. It should be noted here that because only two isotherms were determined, the values of ΔH_p are average values at an intermediate temperature of about 62.5°C. The values of $\Delta S_p^{\pm} - \Delta S_0^{\pm}$ calculated from ΔH_p^{\pm} are given at 50°C, those at 75°C are the same within the accuracy of the calculation. The plots of $\Delta V^{\pm}/V$ for the two temperatures are nearly level up to this point. This indicates that in effect the amount a SnI4 molecule must push back its surroundings in order to diffuse is nearly constant over this range despite the considerable change in free volume. Furthermore, the nearly constant

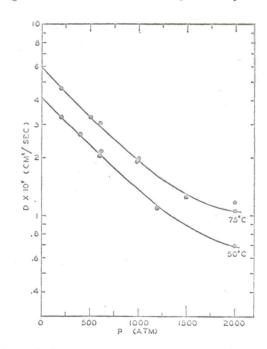


Fig. 1. Diffusion coefficients versus pressure—CCl4-SnI4.