

The Effect of Pressure on Diffusion in the System $\text{CCl}_4-\text{SnI}_4^*$

E. P. DOANE AND H. G. DRICKAMER

Department of Chemistry, University of Illinois, Urbana, Illinois

(Received March 16, 1953)

Diffusion coefficients have been measured for the system $\text{CCl}_4-\text{SnI}_4$ using I^{131} tagged SnI_4 . 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.

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^\ddagger , the activation volume ΔV^\ddagger , and the activation entropy above that at atmospheric pressure $\Delta S^\ddagger - \Delta S_0^\ddagger$.

This paper presents the results of measurements of diffusion of a very dilute solution of SnI_4 (I^{131} tagged) in CCl_4 . The system was chosen because of the simple symmetry of the molecules. The tagged SnI_4 was prepared from iodine received as NaI from the Oak Ridge National Laboratory. I_2 was generated by

50°C and 75°C . The pressure range was limited to 2000 atmospheres because of freezing of CCl_4 . 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, $\Delta V^\ddagger/\bar{V}$, the activation enthalpy ΔH_p^\ddagger , and the increase in activation entropy from 1 to P atmospheres $\Delta S_p^\ddagger - \Delta S_0^\ddagger$ 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^\ddagger are average values at an intermediate temperature of about 62.5°C . The values of $\Delta S_p^\ddagger - \Delta S_0^\ddagger$ calculated from ΔH_p^\ddagger are given at 50°C , those at 75°C are the same within the accuracy of the calculation. The plots of $\Delta V^\ddagger/\bar{V}$ for the two temperatures are nearly level up to this point. This indicates that in effect the amount a SnI_4 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

TABLE I. Diffusion coefficients SnI_4^{131} in $\text{CCl}_4-\text{SnI}_4$ in CCl_4 .

Temperature ($^\circ\text{C}$)	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
75	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 $\text{K}_2\text{Cr}_2\text{O}_7$, and this was reacted with metallic tin in CCl_4 solution as described by McDermott.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 Commission.

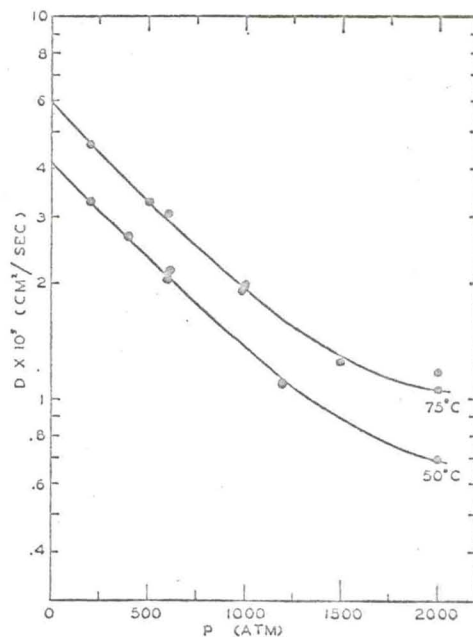
¹ R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 267 (1953).

² R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 575 (1953).

³ Cuddeback, Koeller and Drickamer, J. Chem. Phys. 21, 589 (1953).

⁴ R. B. Cuddeback, and H. G. Drickamer, J. Chem. Phys. 21, 597 (1953).

⁵ F. A. McDermott, J. Am. Chem. Soc. 33, 1963 (1911).

FIG. 1. Diffusion coefficients versus pressure— $\text{CCl}_4-\text{SnI}_4$.