

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

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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

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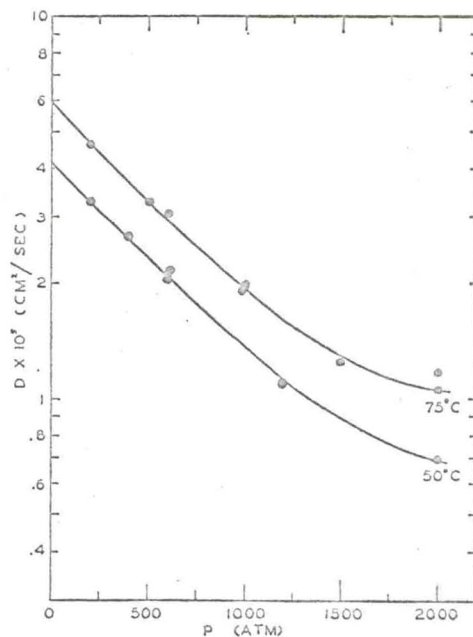
¹ R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 267 (1953).

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— $\text{CCl}_4-\text{SnI}_4$.

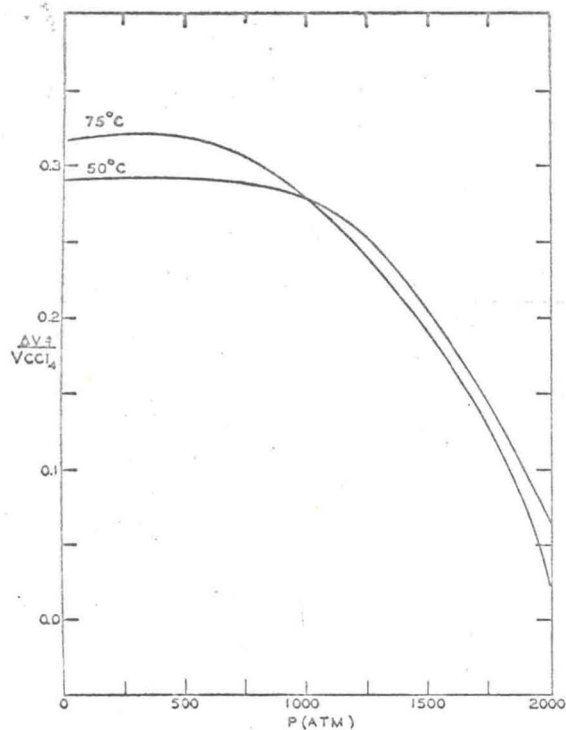


FIG. 2. $\Delta V^\ddagger/V$ versus pressure— CCl_4 — SnI_4 .

low value of ΔH_p^\ddagger shows that the enthalpy of the activated state does not increase relative to that of the normal state. Or, in other words, little energy is expended in accomplishing this volume increase. While

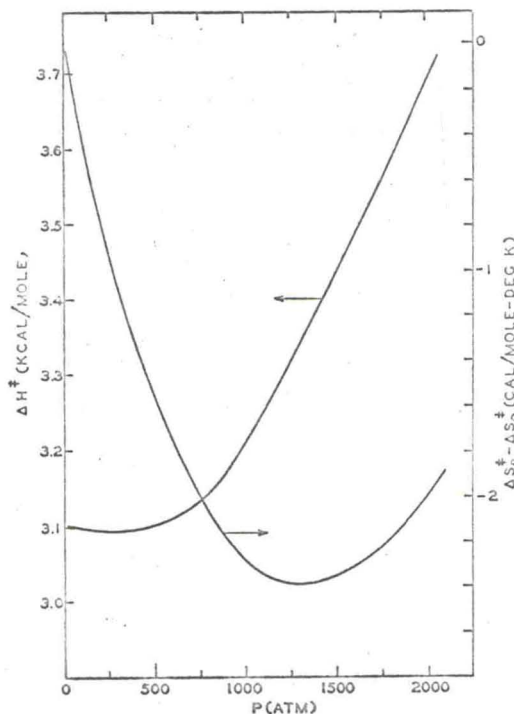


FIG. 3. ΔH^\ddagger versus pressure— CCl_4 — SnI_4 . $\Delta S^\ddagger - \Delta S_0^\ddagger$ versus pressure— CCl_4 — SnI_4 .

both $\Delta V^\ddagger/\bar{V}$ and ΔH_p^\ddagger are changed little, however, I decreases considerably. The reason is found in the $\Delta S_p^\ddagger - \Delta S_0^\ddagger$ curve, which falls rapidly over this region. This means that the entropy of the normal state does not decrease as rapidly as does that of the activated state; that is, the number of degrees of freedom of the activated state are reduced relative to the normal state. Thus the increasing resistance to diffusion over the region below 1000 atmos is apparently caused by the requirement that as pressure increases the SnI_4 molecules must be more stringently oriented in the activated state. This conclusion becomes plausible if we consider the SnI_4 molecules as tetrahedra moving through spheres, or rotating CCl_4 molecules. It is obvious that

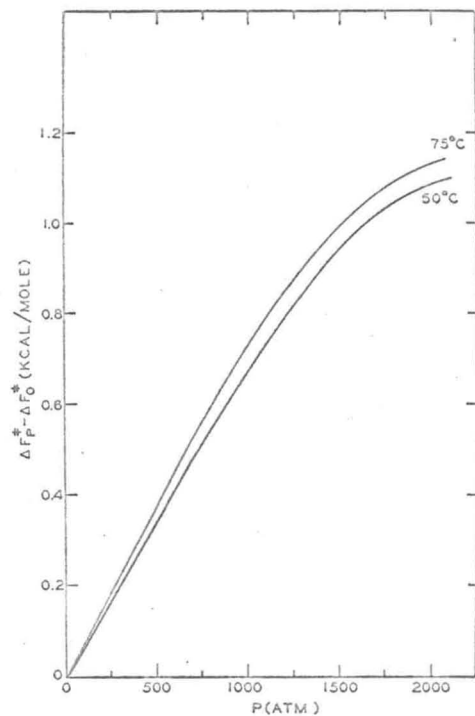


FIG. 4. $\Delta F^\ddagger - \Delta F_0^\ddagger$ versus pressure— CCl_4 — SnI_4 .

in order to diffuse through a medium of closely packed spheres a tetrahedral molecule can move with less distortion of the spheres, on the average, if it is oriented than if it moves without any orientation.

Above 1000 atmos the $\Delta V^\ddagger/\bar{V}$ drops sharply, showing that the amount of distortion needed to move is decreasing. The sudden rise in ΔH_p^\ddagger , however, shows that the energy expended to accomplish this smaller distortion is much greater than at lower pressures. The curve of $\Delta S_p^\ddagger - \Delta S_0^\ddagger$ levels and begins to rise, indicating that the degree of order imposed upon the normal state increases faster than that required of the activated state. The sharp decline in $\Delta V^\ddagger/\bar{V}$ with increasing pressure shows that diffusion is taking place more and more through existing holes, and accordingly indicates

little, however, D is found in the region over this region. In the normal state does not of the activated state of freedom of the molecules in the normal state. Diffusion over the region is caused by the presence of the SnI_4 molecules in the activated state. It is obvious that



$\text{CCl}_4 - \text{SnI}_4$.

of closely packed molecules move with less ease, if it is oriented in a certain direction.

is sharply, showing that molecules are hindered to move is decreased. However, the curve shows that at lower pressures, the smaller distances between molecules in the normal state of the activated state increase with increasing pressure. This indicates that the transition takes place more and more frequently as pressure increases.

at some sort of quasi-static arrangement is appearing in CCl_4 which allows the formation of holes larger than those existing at lower pressures. The most likely explanation seems to be that rotation in the CCl_4 molecules surrounding the SnI_4 molecules begins to be inhibited to some extent at about 1000 atmos at these temperatures. This does not mean that any sharp transition corresponding to the case for the solid at 1000 atmosphere takes place. On the contrary, the nature of the liquid state is such that a sharp transition would not be expected. The intermolecular distances in a liquid are much less uniform than those in a solid. Hence, any such inhibition of rotation would be expected to be a localized phenomenon whose occurrence increases gradually with increasing density. In addition, the present work furnishes no clue as to whether such

an inhibition takes place only around SnI_4 molecules or whether it would take place even in pure CCl_4 . In either event the structure resulting from such an inhibition of the rotation would be expected to be harder to distort, a conclusion supported by the higher values of ΔH_p^\ddagger .

The plots of $\Delta F_p^\ddagger - \Delta F_0^\ddagger$ are shown in Fig. 4. These values are not truly values at 50° and 75°, since they were calculated from the "average" values of $\Delta H_p^\ddagger - \Delta H_0^\ddagger$. The curve shows an increasing value of $\Delta F_p^\ddagger - \Delta F_0^\ddagger$ with P , qualitatively paralleling the decrease in D . This is, of course, to be expected from the manner in which $\Delta F_p^\ddagger - \Delta F_0^\ddagger$ was obtained.

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